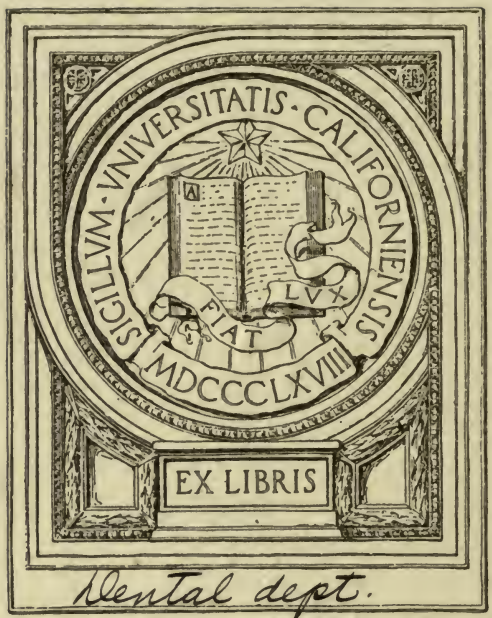
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A TREATISE ON CHEMISTRY

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A

TREATISE ON CHEMISTRY

BY

H. E. ROSCOE F.R.S. AND C. SCHORLEMMER F.R.S.

VOLUME II.—THE METALS

"*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723.

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PREFACE TO VOL. II

(FIRST EDITION)

The aim which the Authors have set before themselves in treating of the Metals and their Compounds is the same as that which they proposed in the discussion of the Non-Metallic Elements. Owing, however, to the large number of the Metals and their Salts, the description of these latter could not, within practicable limits, be made so complete as is possible in the case of the Non-Metallic Compounds. Hence the Authors, whilst giving the characteristic properties of each metal, have been obliged to restrict their notice to those compounds which possess the greatest interest either of a theoretical or practical kind.

Due attention has been paid to the more important technical processes connected with Metallurgy, and no pains have been spared to assist the description of such processes by Drawings of the most modern forms of apparatus and plant.

As an illustration of this the Authors would refer to the Chapter on the Soda and Glass Manufactures in Part I., and to the Metallurgy of Iron in Part II.

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At the end of the volume will be found short Chapters on the Classification of the Elements; on Spectrum Analysis, so far as the detection of terrestrial matter is concerned.

January, 1878.

PREFACE TO THE THIRD EDITION

During the nineteen years which have elapsed since the publication of the first Edition of this volume of the Treatise, much important work on the chemistry of the Metals and their Compounds has been done. So much indeed that a completely New Edition has been prepared, in which the Metallic Elements and their Compounds have been rearranged and all new matter of importance added. I again have to thank my friends Drs. Colman and Harden for the valuable help which they have given me in this as in the last volume.

H. E. ROSCOE.

September, 1897.

PREFACE TO THE FOURTH EDITION

Much new and important matter with regard to the Metals and their Compounds has come to light in the ten years since the last edition of this work appeared, and in the present volume care has been taken to include all the more important points connected with the recent discoveries. The subject of crystallography, which formerly appeared in the first volume, has now been included in the second, and here I must express my thanks to Professor Miers for permitting the use of the illustrations from his own work and for reading the proof of this chapter. Several contributors have assisted in the work of revision; amongst them I must mention Mr. C. O. Bannister, who has written upon Metallurgy and Alloys, Mr. Harry Baker, Dr. Colman, Dr. Marshall Watts, and Mr. Young, who have all assisted in various departments.

H. E. ROSCOE.

September, 1907.

PREFACE TO THE FIFTH EDITION

In preparing the fifth edition of the metals I have to thank several friends for assistance. By their contributions the subject has been brought up to date.

Whilst the general character of the work is preserved several important alterations and additions will be found in this volume. Thus Dr. J. C. Philip has revised and improved the introductory and physical portions, whilst by his reading the whole of the final proofs accuracy has been maintained throughout. Mr. T. V. Barker has re-arranged the chapter on crystallography and has inserted the recent work done in that subject. Dr. Makower has succeeded in placing in clear light the results of the new and important researches in the wide field of radioactivity.

Mr. Bannister, who once more has undertaken the metallurgical portion, Dr. Spencer (Rare Earths), Mr. Baker (Alkali Manufacture), Drs. Keane and Mollwo Perkin (Metallic Compounds) have ably assisted me in their several departments.

It is to be noted that unless a specific statement to the contrary is made all atomic weights are referred to O = 16.

H. E. ROSCOE.

July, 1913.

THE FOLLOWING ARE THE CHIEF CONTRACTIONS EMPLOYED IN THIS VOLUME

Abbreviated Title	Journal
Amer. Chem. J.	American Chemical Journal.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Physik	Annalen der Physik.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Mines	Annales des Mines.
Arch. Néerland.	Archives Néerlandaises des Sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Atti R. Accad. Lincei.	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Biochem. Zeit.	Biochemische Zeitschrift.
Brit. Assoc. Reports	Reports of the British Association.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Soc. chim.	Bulletin de la Société chimique de Paris.
Chem. Centr.	Chemisches Centralblatt.
Chem. News	Chemical News.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Academie des Sciences.
Gazz.	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Chim. phys.	Journal de Chimie physique.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Pharm.	Journal de Pharmacie.
J. Physical Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Journ. Chem. Soc.	Journal of the Chemical Society.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Manch. Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Min. Mag.	Mineralogical Magazine.

Abbreviated Title	Journal
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Phil. Mag.	Philosophical Magazine.
Phil. Trans.	Philosophical Transactions of the Royal Society.
Pogg. Ann.	Poggendorff's Annalen der Physik und der Chemie.
Proc. Chem. Soc.	Proceedings of the Chemical Society.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings [English Version].
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Sitzungsber. K. Akad. Wiss. Berlin	Sitzungsberichte der königlich preussischen Akademie der Wissenschaften zu Berlin.
Zeit. anal. Chem.	Zeitschrift für analytische Chemie.
Zeit. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeit. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeit. Chem.	Zeitschrift für Chemie.
Zeit. Elektrochem.	Zeitschrift für Elektrochemie.
Zeit. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeit. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeit. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

CONTENTS

	PAGE
International Atomic Weights	2
The Metals	3
Determination of the Atomic Weights of the Metals	6
I. Determination of the Equivalent	9
II. Selection of the Atomic Weight	13
Molecular Weights of the Compounds of the Metals	14
Atomic Heat	15
Molecular Heat of Compounds	21
Isomorphism	24
Molecular Weights of the Metals	26
Valency of the Elements	27
Classification of the Elements	42
Natural Arrangement of the Elements	44
The Periodic System	48
Chemical Properties in Relation to the Periodic System	54
Valency in Relation to the Periodic System	55
Physical Properties in Relation to the Periodic System	57
Specific Gravity and Atomic Volume	57
Melting Point	61
Conductivity for Heat and Electricity	64
Correction of Doubtful Atomic Weights	66
Existence of Unknown Elements	68
Crystalline Form of Metals	71
Colloidal Solutions of Metals	72
Alloys and Amalgams	74
Constitution of Salts, Acids, and Bases	90
Metallic Oxides, Hydroxides, and Salts	102
Solubility of Salts	110
Fusibility and Volatility of Salts	121
Generic Properties of Salts	122
Chemical Change and the Law of Mass Action	128

PAGE
Spectrum Analysis 139
Methods of Producing Emission Spectra 145
Mapping and Measuring Spectra 148
Relations between Spectral Lines 155
Application of the Spectroscope to Chemical Analysis 158
Absorption Spectra 163
Crystallography 174
Symmetry of Crystals 182
Enantiomorphism 195
Polymorphism 202
Crystal Structure 204
Chemical Crystallography 208
Mechanical Theories of Crystal Structures 220

SYSTEMATIC DESCRIPTION OF THE METALS AND THEIR DERIVATIVES 224

GROUP I. 224

The Alkali Metals 225
Lithium 227
Sodium 237
The Alkali Manufacture 280
Potassium 318
Rubidium 364
Cæsium 372
Ammonium Compounds 376
Hydroxylamine Salts 395
Hydrazine Salts 396
The Copper Group 398
Copper 398
Silver 445
Gold 490

GROUP II. 528

The Alkaline Earth Metals 529
Calcium 530
Glass 567
Strontium 594
Barium 601
The Magnesium Group 616
Glucinum or Beryllium 616
Magnesium 623
Zinc 642
Cadmium 664
Mercury 671

PAGE

GROUP III. 708

The Aluminium Group 709
Aluminium 710
Earthenware, Pottery, and Porcelain 741
Gallium 751
Indium 754
Thallium 759
Metals of the Rare Earths 772
Scandium 781
Yttrium 782
Lanthanum 785
Cerium 788
Praseodymium 796
Neodymium 798
Samarium 799
Europium 800
Gadolinium 800
Terbium 801
Dysprosium 801
Holmium 801
Erbium 801
Thulium 801
Neo-Ytterbium 802
Lutecium 802
Celtium 802

GROUP IV. 804

The Titanium Group 805
Titanium 805
Zirconium 822
Thorium 830
The Germanium Group 838
Germanium 838
Tin 841
Lead 871

GROUP V. 910

The Vanadium Group 911
Vanadium 911
Columbium or Niobium 944
Tantalum 957
The Antimony Group 962
Antimony 962
Bismuth 998

GROUP VI. 1017

Chromium 1019
Molybdenum 1059
Tungsten 1082
Uranium 1104

PAGE

GROUP VII. 1122

MANGANESE 1123

GROUP VIII. 1160

THE IRON GROUP 1161
IRON 1162
COBALT 1274
NICKEL 1297
THE RUTHENIUM GROUP 1318
RUTHENIUM 1319
RHODIUM 1328
PALLADIUM 1336
THE PLATINUM GROUP 1348
OSMIUM 1349
IRIDIUM 1360
PLATINUM 1371

The Radioactive Elements 1407

PHENOMENA OF RADIOACTIVITY 1416
THE PRODUCTS OF RADIOACTIVE CHANGE 1424
RADIUM 1427
ACTINIUM 1439
THORIUM 1440
URANIUM 1441

INDEX 1449

CHEMISTRY

THE FOLLOWING ARE THE ATOMIC WEIGHTS OF THE ELEMENTS USED IN THIS VOLUME.

1913.

International Atomic Weights.

		O=16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

CHEMISTRY

THE METALS

1 THE metals gold, silver, copper, iron, tin, and lead were known to the ancients. We find them mentioned in the writings of the Old Testament, as well as in those of the early Greek authors. The name of mercury is first found in the writings of Theophrastus, but the existence of most of the remaining metals became known only in comparatively recent times. Antimony appears to have been obtained in very early times, although the reputed Basil Valentine describes its preparation as a novelty, but neither zinc nor bismuth became generally known until the sixteenth century.

An historical notice of each metal will be found under its own heading. We have here simply to consider the progress of our knowledge concerning the properties of the metals as a class.

2 The Latin writer who adopted the name of Geber (Vol. I., p. 7) is the first author in whose writings we find a distinct definition of the word metal: "Metallum est corpus miscibile, fusibile, et sub malleo ex omni dimensione extendibile." According to this definition, mercury, which had been looked upon as metallic by the Greek alchemists, is not included amongst the metals. Geber likewise distinguished gold and silver as the noble metals, because they did not undergo any change in the furnace, whereas the others were termed base metals. This definition was accepted throughout the whole of the middle ages, so that when the brittle metals antimony, bismuth, and zinc came to be well known, they were classed as bastard or semi-metals. Thus, for instance, Paracelsus says: "Zinc, which is a metal and yet no metal, and bismuth and the

like being partly malleable . . . . are bastards of the metals." Opinion was divided respecting the position of mercury, until its solidification by extreme cold, and its malleability in this condition, had been observed in 1759. From this time forward it was universally admitted to be a metal.

The brilliant experiments and reasoning of Lavoisier towards the close of the eighteenth century finally established the elementary nature of the metals, which hitherto had been looked upon by the followers of Stahl as compounded of a calx united with phlogiston (Vol. I., p. 14). In Lavoisier's classification of substances, drawn up in 1787, the metals are grouped together as one of the five classes into which he divided the elements, the distinction between metals and semi-metals being abandoned.

The decomposition of the alkalis by Davy in 1807 made chemists acquainted with substances of an entirely new character. Although the bases of soda and potash agreed "with metals in opacity, lustre, malleability, conductive powers as to heat and electricity, and in their qualities of chemical combination,"[1] and were classed by Davy himself with the metals, yet, inasmuch as they were lighter than water, they were not considered by many chemists to be metals proper. In 1808 Erman and Simon attempted[2] to revive the old distinction between true metals and substances resembling metals by proposing for the new substances the name of metalloids (*μέταλλον* a metal, *εἶδος* similar). This proposal, however, was not generally accepted, and the elements were from this period classed in two groups, the non-metals and the metals, the newly coined term, metalloid, being applied, or rather perhaps misapplied, by Berzelius in 1811 to designate the former of the two classes, in which sense it is still sometimes employed. It soon became evident that the separation of the elements into these two groups was not a logical one, since no satisfactory basis of classification could be obtained. With the discovery of the alkali metals a high specific gravity had ceased to be characteristic, and the property of metallic lustre soon shared its fate. Thus tellurium, discovered in 1782, was grouped with the metals because of its lustre and specific gravity. Its close chemical analogy with sulphur, however, which was pointed out by Berzelius in 1832, clearly indicated that these two elements belonged to the same class.

[1] Davy, *Phil. Trans.*, 1808, **98**, 31. [2] Gilbert's *Annalen*, 1808, **28**, 347.

In the same way, every property supposed to be characteristic of a metal has been found to be shared by some one or other non-metallic substance, or to be absent from some otherwise well-characterised metal. Thus opacity, and the power of conducting electricity well, were long deemed essential properties of a metal ; but we now know that, in very thin layers, metals such as gold and silver are transparent, whilst several non-metals, such as graphite, and selenium, in one of its modifications, conduct electricity like metals.

3 The relations of the so-called non-metals to the metals are well seen when the elements are arranged according to the periodic system (p. 50), which has now superseded the old classification. Thus the elements of the nitrogen group exhibit in a striking manner the gradual transition from a distinctly non-metallic to a distinctly metallic element. Nitrogen itself is undoubtedly a non-metallic body, whilst phosphorus in certain of its allotropic modifications approaches the metals, one of these modifications, indeed, being termed metallic phosphorus. Arsenic, the third member of the nitrogen family of elements, was formerly classed as a semi-metal. At a later period it was considered to be a metal proper, and even now some chemists rank it amongst the metals, whilst others, looking to its striking similarity with phosphorus, place it amongst the non-metals. Antimony and bismuth are elements which belong to this same group, and these substances are always considered to be metals from their close analogy to other distinctly metallic substances. It will be noticed that the members of this group of elements approach more and more closely to a true metal as the atomic weight increases. The same peculiarity is observed in other groups. The elements titanium and zirconium are, on the one hand, closely connected with the non-metal silicon, whilst, on the other, they exhibit the most marked analogies with tin, and are classed accordingly amongst the metals. We must, however, be careful not to draw the conclusion that the elements which possess the highest atomic weights are necessarily metals, and those which possess the lowest are non-metals. Lithium, which after hydrogen and helium possesses the smallest atomic weight, is a well characterised metal, and hydrogen itself exhibits in its chemical relations far more analogy with the metals than with the non-metals ; whilst, on the other hand, xenon, with the atomic weight 130, shows none of the characteristics of a metal.

Although the division into metals and non-metals is thus seen to be one which does not admit of exact definition, it is none the less true that the metals as a class do possess certain generic properties which most of the non-metals either do not possess at all, or exhibit only in a very slight degree. Amongst these properties that of metallic lustre may especially be mentioned. This property is characteristic of all metals, and if it is not noticeable when the metals are in a state of fine division, in which case they frequently appear in the form of black powders, it can readily be observed when the powder is rubbed with a hard body.

Another generic difference which may be noticed is that whilst the characteristic oxides of the non-metals belong to the class of acid-forming oxides, those of the metals are basic in character, only the higher oxides of certain of the metals, as a rule, being capable of forming acids.

DETERMINATION OF THE ATOMIC WEIGHTS OF THE METALS.

4 Although by the year 1819 chemists were in possession of the three principles, laid down respectively by Avogadro, Dulong and Petit, and Mitscherlich, by which they are now guided in the selection of the atomic weights of the elements, yet nearly half a century was to elapse before the establishment of a consistent and generally accepted method of applying these principles.

Avogadro's theory (Vol. I., p. 75), proposed in 1811, a few years only after the introduction of the idea of combination between atoms of characteristic weights, rendered necessary a division of the particles even of elementary substances. The chemists of the period were not, however, prepared to admit the validity of these views, and hence they endeavoured to obtain some other foundation upon which to erect a system of atomic weights. Berzelius (1818) found this in the assumption of the identity of volume and atom in the case of the elementary gases, ascribing to water the formula H_2O, and to oxygen the relative atomic weight 16. In deciding upon the atomic weights of the other elements, especially the metals, Berzelius was forced,[1] like Dalton, to have recourse to purely arbitrary assumptions.

[1] *Essai sur la théorie des proportions chimiques, etc.*, Paris, 1819.

When the important discoveries of Dulong and Petit, and Mitscherlich (Vol. I., p. 42) were made, Berzelius at once saw the simplification which would be effected by the adoption of the theories of these chemists, and in his next table of atomic weights he introduced them consistently, thus arriving at atomic numbers which, with a few exceptions, differ from the modern ones only by small amounts due to the errors of the analytical processes then employed. The chief of these exceptions, potassium, sodium, and silver, were due to the close chemical analogy between the strongly basic oxides of these metals and those of calcium, zinc, etc.; this led Berzelius, in spite of the known specific heat of silver, to formulate them all on the same type RO, the atomic weights assigned to the three metals being therefore twice as great as those now employed.

Dumas, on the other hand, at first based his system of atomic weights on Avogadro's theory, but was seduced from his allegiance to this by a false application of it, which had, however, received the countenance of Avogadro himself. Because the molecules of hydrogen, nitrogen, oxygen, and chlorine were each supposed, according to this theory, to be made up of two atoms, Dumas concluded that the same should be true of the molecules of the vapour of any elementary substance whatever. On this basis he calculated the vapour density of sulphur, but found that the experimental density was three times as great as the theoretical. A somewhat similar inconsistency was observed in the case of phosphorus, and Dumas was thus led to abandon Avogadro's theory, whilst Berzelius was induced by the same experiments to modify his theory of the identity of volume and atom in the case of simple substances, and to confine it to the simple permanent gases.

The discovery of dimorphism in 1823 had rendered the application of Mitscherlich's theory of isomorphism to the selection of atomic weights somewhat uncertain, so that at this time, about 1830, doubts were cast on the possibility of obtaining any satisfactory method of ascertaining the relative weights of the atoms, and it was proposed that chemists should content themselves with employing the equivalent weights directly determined by analysis.

The equivalent system had been proposed in England by Wollaston[1] at a very early date (1814), and had found very general acceptance amongst his countrymen; it had, moreover,

[1] A Synoptic Scale of Chemical Equivalents. *Phil. Trans.*, 1814, **104**, 1.

been adopted by Gmelin in his great *Handbook of Chemistry* (1817), and had thus come into very general use. The tendency to abandon the idea of the chemical atom, as distinct from the equivalent, was moreover strengthened by Faraday's discovery (1834) that the electrolytic equivalents of the metals, that is the relative amounts deposited during a given time by a given current of electricity, are identical with their chemical equivalents.

The rapid development of organic chemistry which occurred in the years 1830–1855 made chemists acquainted with many reactions, such as the formation of mixed ethers (Williamson), acid anhydrides (Gerhardt), and esters, the production of mixed salts of polybasic acids, etc., which could not easily and consistently be formulated on the basis of the equivalent system. Numerous modifications of the system were therefore introduced by individual investigators, until it became quite impossible to interpret a chemical formula without special information as to the sense in which the symbols were employed by the particular author in question.

A most important proposal was put forward by Gerhardt, who along with Laurent, had resuscitated Avogadro's theory, and applied it consistently to all volatile compounds. He regarded all the basic oxides of the metals as derived from water by the replacement of the hydrogen by two atoms of the metal, the general formula of the oxides being R_2O. Silver, potassium, and sodium thus received the atomic weights which are now recognised, whilst the atomic weights of metals such as lead, zinc, calcium, etc., had only one-half of the modern values.

In 1858, the various conflicting systems were finally co-ordinated by Cannizzaro[1] in his *Sketch of a Course of Chemical Philosophy*. In this admirable paper, which is one of the classics of chemical literature, he pointed out in detail how a complete and consistent system of formulæ could be obtained by the recognition both of Avogadro's theory, and the theory of atomic and molecular heats as founded by Dulong and Petit, Neumann, and Joule. In the case of metals which form compounds volatile without decomposition, Cannizzaro was able to show that the

[1] Sunto di un corso di filosofia chimica fatto nella Reale Università di Genova del Professore S. Cannizzaro, Nuovo Cimento (1858), VII. An English translation of this paper has been published as No. 18 of the *Alembic Club Reprints*. Reference may be made also to the Cannizzaro Memorial Lecture, by Sir William Tilden, *Journ. Chem. Soc.*, 1912, **101**, 1677.

atomic weight deduced from specific heat was in agreement with the value deduced from vapour density. The atomic weights suggested by Cannizzaro were gradually adopted by chemists as soon as they realised the simplicity and consistency of the system, and they are the ones still employed. One of the immediate results flowing from the adoption of Cannizzaro's numbers was the periodic system of classification of the elements introduced by De Chancourtois, Newlands, Mendeléeff, and Lothar Meyer (see p. 44).

5 The determination of the atomic weight of an element involves, as has already been pointed out (Vol. I., p. 77), two processes:—(1) The determination of the proportion by weight in which the element combines with other elements, or, as it is called, the chemical equivalent of the element; (2) The selection of that multiple of the equivalent which represents the smallest amount of the element found in a molecule, and which is known as its *atomic weight.*

I. Determination of the Equivalent.

6 In expressing the chemical equivalents of the elements, it is convenient to have some one element as the standard of reference, and formerly hydrogen was chosen for this purpose. Since, however, comparatively few of the metals form well-defined compounds with hydrogen, the equivalent of a metal referred to hydrogen had in nearly all cases to be calculated from an analysis of the compounds of the metal with oxygen or chlorine. Accordingly, it is now generally agreed that oxygen should be taken as the standard element (Vol. I., p. 78). On this basis the equivalent of an element is defined as the number of parts by weight of the element which combine with 8 parts by weight of oxygen. Our knowledge of the quantitative relation between hydrogen and oxygen (Vol. I., p. 284) on the one hand, and hydrogen and chlorine (Vol. I., p. 212) on the other, permits an extension of the definition in the following terms: the equivalent of an element is the number of parts by weight of the element which combine with 1·008 parts by weight of hydrogen or 35·46 parts by weight of chlorine. Elements which combine with any of the standards in several different proportions have, of course, a corresponding number of different equivalents.

The equivalent of an element can be most directly determined

by the analysis or synthesis of its oxide, a process which gives immediately the proportion by weight in which the element combines with oxygen. Thus the equivalents of nickel and iron have been determined by reducing a weighed amount of the oxide to the corresponding metal, whilst the inverse process of converting the metal into an oxide has been employed in determining the equivalents of antimony and of bismuth. In most cases, however, this direct process cannot be applied, and recourse is then had to indirect methods of analysis or synthesis. Thus the chlorides of the metals cannot, as a rule, be directly analysed or synthesised with great quantitative accuracy; it is therefore usually more convenient and accurate to bring a weighed amount of the chloride into reaction with a salt of silver, and ascertain either the amount of silver required to combine with the whole of the chlorine present, or the weight of silver chloride produced, or both of these quantities. When this is known, the amount of chlorine present, and therefore the composition of the chloride, can be calculated, provided that the ratio in which silver unites with chlorine, *i.e.*, the composition of silver chloride, be known.

Stas found, for example, that 85·031 parts of sodium chloride required 156·862 parts of silver for the complete precipitation of its chlorine in the form of silver chloride. Since 107·12 parts of silver were found by him to be equivalent to 1 of hydrogen, and to combine with 35·18 of chlorine to form silver chloride, it follows that the amount of sodium chloride which is required to react with 107·12 parts of silver, and therefore contains 35·18 parts of chlorine, is $\frac{85{\cdot}031 \times 107{\cdot}12}{156{\cdot}862} = 58{\cdot}06$. Hence $58{\cdot}06 - 35{\cdot}18 = 22{\cdot}88$ parts of sodium are equivalent to 107·12 parts of silver, or 1 part of hydrogen. This conclusion, if re-stated on the basis of the oxygen standard, would run: 23·06 parts of sodium are equivalent to 107·98 parts of silver or 8 parts of oxygen.

In a similar way, the equivalent of an element may be indirectly ascertained by estimating the amount of any substance required for, or produced in, a reaction in which a weighed amount of the element or one of its compounds takes part. The equivalents of a very large number of the metals have accordingly been ascertained by the conversion of an oxide into a salt, of a salt into an oxide, or of one salt into another. Thus, for example, Erdmann and Marchand found that 100 parts of calcium carbonate yield 136·05 parts of calcium sulphate. From

the known composition and properties of carbonic acid gas and sulphur trioxide, it follows that an increase of weight of 35·80 in this reaction corresponds with 43·67 parts of carbonic acid gas in the original carbonate, and, further, that this is combined with such a quantity of an oxide as contains 15·88 parts of oxygen. Hence 100 parts of calcium carbonate, which gain 36·05 in the reaction, contain $\frac{43{\cdot}67 \times 36{\cdot}05}{35{\cdot}80} = 43{\cdot}99$ parts of carbonic acid gas, combined with 56·01 parts of calcium oxide, and this contains $\frac{15{\cdot}88 \times 36{\cdot}05}{35{\cdot}80} = 16$ parts of oxygen, and 40·01 of calcium. Hence, according to this particular experiment, the equivalent of calcium is $\frac{40{\cdot}01 \times 8}{16} = 20{\cdot}005$. The equivalent of calcium can also be similarly deduced from the results obtained by the same chemists for the calcination of calc-spar, 13·6031 grams of which were found to yield 7·6175 grams of quicklime on ignition.

In other cases the amount of hydrogen which is evolved when a weighed amount of a metal is dissolved in an acid or alkali (aluminium, zinc), the amount of a metal precipitated by a weighed amount of another metal from a solution of one of its salts, the amount of metal deposited by the electrolysis of a weighed amount of a salt (copper), the amount of an acid required to neutralise a weighed amount of a given base, may be used for the determination of the equivalent, provided that the necessary knowledge of the equivalents of the various other substances involved is available.

In all these indirect processes, in addition to the unavoidable experimental error of the actual estimation, there is also the experimental error involved in each of the equivalents employed in the calculation. The investigator, therefore, in selecting methods for the determination of the equivalent of an element, will, if possible, choose such as involve substances of which the equivalents are known with the greatest accuracy. The experimental error of the actual estimation cannot be entirely removed, but its effect is diminished by taking the average result of a large number of experiments, and by arranging that the amount of material employed shall be sufficiently large to make this inevitable error bear as small a ratio as possible to the number which is to be determined. A further precaution, which should always be taken when it is practicable, is to

determine the equivalent by as many distinct processes as possible, since in this way the special experimental error which is peculiar to each process is to some extent eliminated.

The experimental foundation which is thus seen to be necessary for the construction of a system of equivalents is due in great part to the classical labours of Stas,[1] who carried the processes of analytical chemistry to a degree of accuracy quite unknown to his predecessors, Dalton, Berzelius, and Dumas. Stas chose silver as the substance which was most convenient for experimental purposes, and determined its equivalent on the one hand to oxygen, and on the other to chlorine, bromine, iodine, sulphur, and potassium, very great precautions being taken to avoid error. The equivalent of silver to chlorine, bromine, and iodine was determined by the direct synthesis of the corresponding compound. In the case of chlorine, the silver and the silver chloride obtained from it were weighed; on the other hand, the compositions of the bromide and iodide were determined by a series of complete syntheses, the metallic silver, the bromine or iodine, and the silver bromide or iodide being all weighed. The equivalent of silver to oxygen was ascertained by the reduction of silver chlorate, bromate, and iodate to the chloride, bromide, and iodide. The difference in weight between the oxygenated salt which was taken and the halogen compound which was obtained gives the ratio of oxygen to silver chloride, etc., and the composition of the latter having been ascertained as just described, the ratio of silver to oxygen can be calculated. In another series of experiments designed for the same purpose, potassium chlorate was converted into potassium chloride by heat, and the ratio of potassium chloride to oxygen thus obtained. The amount of silver necessary to combine with the chlorine of a weighed amount of potassium chloride was then determined, and the ratio silver : potassium chloride : oxygen thus ascertained. A similar series of experiments was carried out with the sulphide and sulphate of silver. In this way, then, the equivalents of silver, chlorine, bromine, iodine, sulphur, and potassium, relatively to oxygen, were all obtained, and these were used by Stas for the determination of the equivalents of sodium, lithium, lead, and nitrogen.

The probable error in the mean equivalent of silver deduced

[1] Nouvelles recherches sur les lois des proportions chimiques ; sur les poids atomiques et leur rapports mutuels (Bruxelles, 1865).

from these five sets of experiments amounts to only 0·0034 per cent. Recent investigations, however, tend to show that, in spite of the great care exercised by Stas, certain errors were not avoided, and that the numbers obtained by him require correction. Within the last six or seven years the fundamental ratios have been subjected to very careful revision by a number of workers, and the result has been that the values adopted by Stas have been altered to a slight extent. The most probable value, for example, of the ratio Ag : AgCl is now taken as 100 : 132·87, instead of 100 : 132·85, found by Stas. The adoption of corrected values for the fundamental ratios has rendered necessary alterations in those atomic weights which have been calculated with the aid of the ratios. The changes which have been agreed on are all incorporated in the table of atomic weights on p. 2, and a summary of the work which has led to the adoption of these changes will be found in the Reports of the International Committee on Atomic Weights.[1]

The special methods adopted for the determination of the equivalents of the various metals will be found under their several headings.

II. Selection of the Atomic Weight.

7 The methods already described (Vol. I., p. 77) for the determination of the atomic weight of an element by ascertaining the molecular weights of a number of its compounds by the vapour density method, and then finding out by comparison the smallest amount of the element which is ever present in a molecule, may be applied without alteration to such of the metals as form volatile compounds. Many metals, however, form such a small number of volatile compounds that the determination of the atomic weight by this method becomes unsatisfactory, and, of course, it cannot be applied at all to such of the metals as do not form volatile compounds. The molecular weights both of the metals themselves and of their compounds in solution in various solvents may in certain cases be ascertained either by the cryoscopic method of Raoult, or by the boiling point method (Vol. I., p. 132).

[1] *Proc. Chem. Soc.*, 1906, **22**, 2; 1907, **23**, 2; 1908, **24**, 2; 1909, **25**, 3; *Journ. Chem. Soc.*, 1909, **95**, 2216; 1910, **97**, 1861; 1911, **99**, 1867; 1912, **101**, 1830.

In cases to which none of these methods can be applied chemists are guided by the specific heat of the metal and its compounds, its general relations with the other elements, and the isomorphism of its compounds.

Molecular Weights of the Compounds of the Metals.

8 The most volatile among the compounds of the metals are the organo-metallic derivatives, which may be looked upon as compounds of the metals with the alcohol radicals. They are usually obtained by the action of a metal on an organic iodide, zinc-methyl, for example, being prepared by the action of zinc on methyl iodide:

$$2Zn + 2CH_3I = ZnI_2 + Zn(CH_3)_2.$$

These compounds are usually liquids which boil at comparatively low temperatures, and their vapour densities can therefore be determined by the ordinary methods, except that, as they are very readily oxidised and are usually spontaneously inflammable, the determinations must be carried out in an atmosphere of an indifferent gas, such as nitrogen. In addition to these compounds of the metals with the alcohol radicals, the remarkable compounds of nickel and iron with carbonic oxide, and the metallic derivatives of acetylacetone, serve for the same purpose. Volatile organic compounds, the vapour densities of which have been determined, are formed by the following metals: Zn, Hg, Al, Sn, Pb, Sb, Bi, Ge, Mn, Cr, Co, Mo, Fe, and Ni.

Further, many metals form halogen compounds which volatilise at moderate temperatures, and the vapour density of which can therefore be determined. In a few cases, the vapour density of the metal itself has been found to be of value in deciding upon the atomic weight.

The experimental methods of ascertaining the vapour density of substances which are volatile only at high temperatures differ somewhat from those ordinarily employed. The older determinations of Deville and Troost, Roscoe, and others, were carried out by Dumas's method, a bulb of porcelain, which can be sealed by means of the oxy-hydrogen jet, being used for temperatures above that at which glass softens. The great difficulty inherent in this process is the determination of the temperature, which must be known with considerable accuracy. This was determined either calorimetrically, by the aid of a

weighed mass of platinum, or by the use of a second similar bulb containing iodine or mercury, the temperature being calculated from the amount of vapour left in this second bulb under the conditions of the experiment. This process has now been superseded by that of Victor Meyer, which was originally introduced for this purpose, and presents the great advantage that a knowledge of the temperature of the experiment is not involved in the calculation of the results. An apparatus constructed of, or lined with, porcelain, platinum, or iridium, is employed, and is heated to the requisite temperature either by the vapour of some substance of high boiling point, or by a gas- or electric-furnace. It is of course essential that the temperature of the apparatus be maintained constant throughout the duration of the experiment. The air in the apparatus is usually displaced by nitrogen, to prevent the oxidation which would otherwise occur in many cases at the high temperature employed. A modification of Victor Meyer's method, suitable for temperatures about 2000° C., and involving the use of very small quantities of material, has been devised by Nernst.[1]

The interpretation of the experimental results is often rendered difficult by the complete or partial dissociation of the compound, either into two similar or two dissimilar molecules. The occurrence of this is rendered evident by the fact that the vapour density varies with the temperature at which it is determined. Several cases of this kind are discussed in connection with the subject of valency.

Atomic Heat.

9 The specific heat of a body is the ratio of the quantity of heat required to raise the temperature of the body 1° to the quantity required to raise that of an equal weight of water 1° (Maxwell). The amount of heat needed to raise a kilogram of water through 100° is thirty-one times as large as that required to raise the same weight of platinum through the same interval of temperature, or, in other words, the amount of heat which raises one kilogram of water through 100° will raise thirty-one kilograms of platinum over the same range; hence the specific heat of platinum is said to be $\frac{1}{31} = 0{\cdot}032$. The specific heat of the same substance varies considerably under different

[1] *Zeit. Elektrochem.*, 1903, 9, 622.

physical conditions and according as the substance is solid, liquid, or gaseous.

A careful determination of the specific heat of thirteen of the solid elements by Dulong and Petit in the year 1819 [1] showed that a simple relation existed between the chemical equivalent and the specific heat of these substances. When the numbers representing these two quantities for each element were multiplied together, the products were found either to be equal, or to stand in a very simple ratio. By a supposition analogous to that made by Avogadro with respect to the combination of gases by volume, Dulong and Petit concluded that the specific heat of the metals varied inversely as the atomic weight, and proposed to adopt as the relative atomic weights of the metals those numbers which, multiplied by the specific heat, gave a constant product. Having thus modified the atomic weights which were current at that time, the French experimentalists formulated the proposition that *the atoms of different elements possess the same capacity for heat*, or *all the elements have the same atomic heat.* Although chemists at the time acknowledged the importance of this generalisation, they did not regard it as established beyond doubt, inasmuch as the alterations in the atomic weights introduced by Dulong and Petit, although admissible in some cases, led in other respects to very improbable conclusions. Moreover, a few of the elements investigated by the French chemists were very impure, so that the specific heats which they obtained were inexact. Berzelius very properly insisted that further investigation was necessary, and added,[2] "If we attempt to apply this idea to compound bodies, and if the result of such an examination confirms the views of Dulong and Petit, this discovery will rank as one of the most important parts of theoretical chemistry."

The next step in the direction thus indicated by Berzelius was made by F. Neumann,[3] who showed that equivalent quantities of similarly constituted compounds require equal quantities of heat to raise their temperature by the same amount, and that this equality is independent of difference in crystalline form; thus calc-spar and aragonite possess the same specific heat. Neumann, however, did not connect this discovery of the relation between the specific heats of the compounds with that of Dulong and Petit respecting the specific heats of the

[1] *Ann. Chim. Phys.*, 1819, **10**, 395.
[2] Berzelius's *Jahresb.*, 1822, **1**, 19. [3] *Pogg. Ann.*, 1831, **23**, 1.

elements. Only by degrees, and in the hands of numerous observers, was this connection established, and even at the present day it cannot be said that the subject is fully investigated. The researches which have mainly contributed to the development of the subject are those of Hermann, 1834, Regnault, 1840, De la Rive and Marcet, 1840, Joule, 1844, Woestyn, 1845, Garnier, 1852, Cannizzaro, 1858, H. Kopp, 1864[1] (whose memoir contains an historical introduction to the whole subject).

It is especially to the researches of Regnault and Kopp that we are indebted for the corroboration of the results of the earlier experiments proving that the rule of Dulong and Petit is applicable with a very considerable degree of accuracy to about forty of the elementary bodies, when the mean specific heats of the solid elements between 0° and 100° are employed. We may, therefore, regard those weights of the elements as their atomic weights which, when multiplied into the specific heats of the elements, give a constant number. This number represents the capacity of the atom for heat, or the *atomic heat* of the element, and its value for most of the elements lies near 6·3. This is clearly seen if we multiply the specific heats of a few metals by their corresponding atomic weights, for example :—

	Specific heat.		Atomic weight.		Atomic heat.
Lead . . .	0·0310	×	207·1	=	6·4
Platinum . .	0·0323	×	195·2	=	6·3
Silver . . .	0·0562	×	107·98	=	6·1
Tin	0·0551	×	119·0	=	6·6
Zinc . . .	0·0935	×	65·4	=	6·1

This relationship may therefore be employed for the purpose of controlling the determinations of atomic weight in doubtful cases. Amongst those elements which conform to the theory are in the first place the metals, and then certain non-metals, such as bromine, iodine, selenium, tellurium, and arsenic.

The following table shows within what limits the atomic heat of the different elements varies. The first column contains the names of the elements, the second their mean specific heats for the range of temperature given in the third, the fourth the atomic weight, the fifth the product of the atomic weight into the specific heat, and the sixth the names of the observers :—

[1] *Annalen*, 1864, Suppl. **3**, 1.

I.	II.	III.	IV.	V.	VI.
Lithium . . .	0·9408	27° to 99°	6·94	6·5	Regnault.
Sodium	0·2934	− 28 ,, 6	23·00	6·7	,,
Magnesium . .	0·2460	18 ,, 99	24·3	6·0	Voigt.
Aluminium . .	0·2189	15 ,, 185	27·1	5·9	Tilden.
Phosphorus . .	0·202	13 ,, 36	31 0	6·3	Kopp.
Sulphur. . . .	0·1844	15 ,, 97	32·1	5 9	Regnault.
Potassium. . .	0·1662	− 78·5 ,, 23	39·1	6·5	Schüz.
Calcium . . .	0·149	0 ,, 100	40·1	6·0	Bernini.
Titanium . .	0·1125	0 ,, 100	48·1	5·4	Nilson and Pettersson.
Vanadium . .	0·1153	0 ,, 100	51·0	5·9	Mache.
Chromium . .	0·1208	0 ,, 100	52·0	6·3	,,
Manganese . .	0·1217	14 ,, 97	54·9	6·7	Regnault.
Iron	0·1162	23 ,, 100	55·8	6·5	Trowbridge.
Cobalt	0·1030	15 ,, 100	59·0	6·1	Tilden.
Nickel	0·1084	15 ,, 100	58·7	6·4	,,
Copper	0·0936	20 ,, 100	63·6	6·0	Schmitz.
Zinc	0·0935	0 ,, 100	65·4	6 1	Bunsen.
Gallium. . . .	0·079	12 ,, 23	69·9	5·5	Berthelot.
Germanium . .	0·0737	0 ,, 100	72·5	5·3	Nilson and Pettersson.
Arsenic	0·0830	21 ,, 68	75·0	6 2	Bettendorf & Wüllner.
Selenium . .	0·0840	22 ,, 62	79·2	6·7	,, ,,
Bromine . . .	0·0843	− 78 ,, − 20	79·9	6·7	Regnault.
Zirconium . .	0·0660	0 ,, 100	90·6	6·0	Mixter and Dana.
Molybdenum .	0·0647	20 ,, 100	96·0	6·2	Stücker.
Ruthenium . .	0·0611	0 ,, 100	101·7	6·2	Bunsen.
Rhodium . . .	0·0580	10 ,, 97	102·9	6·0	Regnault.
Palladium . .	0·0593	10 ,, 100	106·7	6·3	,,
Silver	0·0562	15 ,, 100	107·9	6·1	Bartoli and Stracciati.
Cadmium . . .	0·0548	0 ,, 100	112·4	6·2	Bunsen.
Indium	0·0569	0 ,, 100	114·8	6·5	,,
Tin	0·0551	20 ,, 109	119·0	6·6	Spring.
Antimony . .	0·0495	0 ,, 100	120·2	5·9	Bunsen.
Tellurium . . .	0·0483	− 15 ,, 100	127·5	6·2	Tilden.
Iodine	0·0541	9 ,, 98	126·9	6·9	Regnault.
Cæsium . . .	0·048	0 ,, 26	132·8	6·4	Erkardt and Graefe.
Lanthanum . .	0·0448	0 ,, 100	139·0	6·2	Hillebrand.
Cerium	0·0448	0 ,, 100	140·2	6·3	,,
Tantalum . .	0·0363	16 ,, 100	181·5	6·6	von Bolton.
Tungsten . . .	0·0336	0 ,, 100	184·0	6·2	Mache.
Osmium . . .	0·0311	19 ,, 98	190·9	5·9	Regnault.
Iridium	0·0323	18 ,, 100	193·1	6·2	Behn.
Platinum . . .	0·0323	0 ,, 100	195·2	6·3	Bunsen.
Gold	0·0316	0 ,, 100	197·2	6·2	Violle.
Mercury . . .	0·0319	− 78 ,, − 40	200·6	6·4	Regnault.
Thallium . . .	0·0326	20 ,, 100	204·0	6·6	Schmitz.
Lead	0·0310	18 ,, 100	207·1	6·4	Behn.
Bismuth . .	0·0304	17 ,, 99	208 0	6·3	Voigt.
Thorium . . .	0·0276	0 ,, 100	232·4	6·4	Nilson.
Uranium . . .	0·0280	0 ,, 98	238·5	6·7	Blümcke.

10 The following elements, the atomic heats of which are less than 5, have been omitted from the foregoing table :—

I.	II.	III.	IV.	V.	VI.
Glucinum . . .	0·4246	0° to 100°	9·1	3·9	Nilson and Pettersson.
Boron . . .	0·3066	0 ,, 100	11·0	3·4	Moissan and Gautier.
Diamond . . .	0·1461	0 ,, 99·8	12·0	1·8	Weber.
Graphite . . .	0·1904	0 ,, 99	12·0	2·3	,,
Wood charcoal	0·1935	0 ,, 99	12·0	2·3	,,
Gas carbon . .	0·2040	24 ,, 68	12 0	2·4	Bettendorf & Wüllner.
Silicon	0·1730	14 ,, 97	28·3	4·9	Regnault.

These elements accordingly possess at temperatures between 0° and 100° smaller atomic heats than correspond to Dulong and Petit's rule. Weber's investigations[1] have shown that the specific heat of carbon varies very considerably with the temperature, but that above a certain limit of temperature it remains constant and then agrees with Dulong and Petit's rule; this is seen in the following table, in which the true specific heats at the temperatures quoted are given:—

	Temperature.	Specific heat.	Atomic heat.
Diamond . . .	−50·5°	0·0635	0·76
,, . . .	+10·7	0·1128	1·35
,, . . .	58·3	0·1532	1·84
,, . . .	140·0	0·2218	2·66
,, . . .	206·1	0·2733	3·28
,, . . .	606·7	0·4408	5·29
,, . . .	806·5	0·4489	5·39
,, . . .	985·0	0·4589	5·51
Graphite . . .	−50·3	0·1138	1·37
,, . . .	+61·3	0·1990	2·39
,, . . .	641·9	0·4454	5·34
,, . . .	977·9	0·4670	5·60

Similar results have been obtained in the case of silicon. The specific heat of this element increases from 0·1360 at −39·8° to 0·2029 at 232°, above which it appears to remain constant, the atomic heat then being 5·7. Boron also exhibits the same phenomenon, the specific heat increasing from 0·1965 at −39·6° to 0·3663 at 233°, and probably becoming constant at 500–600°.

The same investigator has shown also that the allotropic modifications of a substance at low temperatures possess different

[1] *On the Specific Heat of the Elements Carbon, Boron, and Silicon* (Stuttgart, 1874).

specific heats, but that this difference diminishes as the temperature rises, and at last altogether disappears. For example, Regnault concluded from his experiments that the specific heat of amorphous carbon was different from that of the two other modifications. Weber has, however, distinctly shown that this is not the case, but that carbon exists in only two thermal modifications, (1) opaque, (2) transparent. These thermal differences occur only at low temperatures, and when a high temperature is reached no variation is observed.

11 From the table (p. 18) we see that the atomic heats of the elements differ from one another considerably, even within the limits of temperature at which these values have been obtained. Thus, for instance, whilst the value for the majority lies between 6·1 and 6·6, in others the number sinks so low as 5·3, and in the case of iodine exceeds 6·7. These differences may perhaps in some instances be explained by the fact that the substances under investigation were impure. It must also be remembered that the specific heat of most substances varies with the temperature, and the researches of Pionchon,[1] Behn,[2] Tilden,[3] and others,[4] have shown that this variation, even for the metals, is often very considerable. This is well seen in the following table, in which the true specific and atomic heats of a number of metals are given for a series of temperatures:— [5]

Absolute temperature.	Aluminium.		Nickel.		Silver.		Tellurium.	
	Specific heat.	Atomic heat.	Specific heat.	Atomic heat.	Specific heat.	Atomic heat.	Specific heat.	Atomic heat.
100°	0·1226	3·32	0·0575	3·37	0·0467	5·04	0·0462	5·89
200	0·1731	4·69	0·0878	5·15	0·0528	5·70	0·0471	6·00
300	0·2053	5·56	0·1054	6·18	0·0558	6·02	0·0480	6·12
400	0·2254	6·11	0·1168	6·85	0·0572	6·17	0·0489	6·23
500	0·2384	6·46	0·1233	7·24	0·0581	6·27	0·0498	6·35
600	0·2471	6·70	0·1275	7·48	0·0587	6·33	0·0507	6·46
700	0·2531	6·86	0·1301	7·63	0·0590	6·37	0·0516	6·58
800	—	—	0·1321	7·75	—	—	—	—
900	—	—	0·1338	7·85	—	—	—	—

[1] *Compt. rend.*, 1886, **102**, 1122.

[2] *Ann. Physik*, 1901, [4], **1**, 257.

[3] *Phil. Trans.*, 1900, **194**, 23; 1903, **201**, 38; 1904, **203**, 143.

[4] Wigand, *Ann. Physik*, 1907, **22**, 99; Magnus, *ibid.*, 1910, **31**, 597; Richards and Jackson, *Zeit. physikal. Chem.*, 1910, **70**, 414; Schimpff, *ibid.*, 1910, **71**, 257.

[5] Tilden, *Journ. Chem. Soc.*, 1905, **87**, 555. Here, as in other tables of this section, the values of the atomic heat have been recalculated on the basis of the revised figures for the atomic weights of the elements.

It appears from this that no better agreement is obtained by determining the specific heat at a temperature at which the variation with temperature is small, than by adopting the usual method of taking the mean specific heat for a range of temperature from 0° to 100°.

The original statement of Dulong and Petit as to the identity of the atomic heats of the elements can therefore be regarded as only a rough approximation, applicable mainly to the metals between 0° and 100°.[1]

We must bear in mind that when we speak of specific heat, we really refer to a complex quantity, comprising not only the heat which actually goes to raise the temperature of the heated body, but also that which is expended in performing external or internal work, such as expansion, or diminution of the cohesion of the particular body. This last amount of heat is different for different substances, whilst the first amount is theoretically the same for a molecule of any substance.

The above generalisation does not apply to liquid or gaseous elements with the single exception of mercury, which possesses almost the same atomic heat in the liquid as in the solid state.

The most important evidence for the applicability of Dulong and Petit's rule is the fact that the results deduced from it agree with those deduced from Avogadro's theory for those metals which form volatile compounds, and with which, therefore, such a comparison can be instituted.

Molecular Heat of Compounds.

12 The law that the molecular heat of a compound is equal to the sum of the atomic heats of its elements, or that the atomic heat of an element does not undergo change when that element enters into combination, was first laid down by Joule,[2] but its experimental verification is chiefly due to Kopp. The following examples will illustrate this:—

		Specific heat.	Molecular heat.	
			Found.	Calculated.
Potassium bromide	KBr	0·1070	12·7	13·2
Mercuric iodide .	HgI_2	0·0423	19·2	20·2
Lead iodide . . .	PbI_2	0·0427	19·7	20 2
Lead bromide . .	$PbBr_2$	0·0533	19·6	19·8

[1] Compare Lewis, *J. Amer. Chem. Soc.*, 1907, **29**, 1165; Nernst, *Zeit. Elektrochem.*, 1911, **17**, 265.

[2] *Phil. Mag.*, 1844, [3], **25**, 334.

This agreement, moreover, is maintained at varying temperatures, so that the specific heat of each of the elements in a compound varies with the temperature in the same way as it does when the element itself is heated. This is shown in the following table for nickel telluride, NiTe, the calculated figures being obtained by adding together the atomic heats of nickel and tellurium given on p. 20.[1]

Absolute temperature.	Molecular heat. Observed.	Calculated.
100°	8·44	9·26
200	11·43	11·15
300	12·50	12·30
400	13·01	13·08
500	13·24	13·59
600	13·37	13·94
700	13·45	14·21

Hence if the atomic heat of a solid element has not been determined, it may be calculated from the molecular heat of its compounds with other elements whose atomic heats are known. In this way the atomic heats of rubidium, strontium, barium, and titanium have been determined at various times, and the values so found agree with the rule which comprises all the other metals.

Kopp has shown also that the elements which are gases at the ordinary temperature possess a constant atomic heat in their various solid compounds. On this basis the atomic heat of chlorine has been found to be 5·9, that of nitrogen 5·3, of fluorine, 5·0, of oxygen 4·0, and of hydrogen 2·3. The following examples illustrate this point:—

		Specific heat.	Molecular heat. Found.	Calculated.
Silver chloride	$AgCl$	0·089	12·7	12·0
Zinc chloride	$ZnCl_2$	0·136	18·5	17·9
Potassium platinichloride	K_2PtCl_6	0·118	57·4	54·7
Ice	H_2O	0·478	8·6	8·6
Mercuric oxide	HgO	0·048	10·4	10·4
Calcium carbonate	$CaCO_3$	0·206	20·6	20·7
Potassium sulphate	K_2SO_4	0·196	34·2	34·9
Hexachlorethane	C_2Cl_6	0·177	41·9	39·2

[1] Tilden, *Journ. Chem. Soc.*, 1905, **87**, 557.

Kopp has moreover proved that the elements boron, silicon, and carbon possess, in combination, the same atomic heat as in the free state, at temperatures below 100°C. This renders it probable that, if we could obtain the specific heat of oxygen and hydrogen compounds at a high temperature, the atomic heats of these elements would exhibit the same sort of alteration which has been proved to occur in the case of carbon, silicon, and boron.

In the case of oxygen such a change has actually been deduced from experiments on the specific heats of the metallic oxides by Tilden, who has calculated from the temperature variation of the specific heat of alumina, Al_2O_3, that the atomic heat of combined oxygen is 1·9 at 100° Abs., 3·3 at 300°, 3·8 at 500°, and 4·0 at 700°. These results lead to the value 3 for the atomic heat of combined oxygen at about 0° C., and hence it follows, since the specific heat of ice between −78° and 0° is 0·47, that the atomic heat of combined hydrogen is 2·7. These numbers differ somewhat from those of Kopp given above.

13 Taking into consideration the results thus deduced from the molecular heats of compounds, it appears that the elements which possess an exceptionally small atomic heat at temperatures below 100° have low atomic weights and, with the exception of glucinum, are non-metals (see p. 9). All the non-metals whose atomic weights are high, as well as the remaining metals, agree approximately with Dulong and Petit's rule below 100°C.

14 As instances of the employment of the atomic heat in selecting the atomic weight, the following may be quoted.

Thallium shows many analogies on the one hand with the alkali metals, and on the other with lead, and it was for some time a matter of doubt whether the lower chloride should be formulated as $TlCl_2$, in which case the atomic weight would be 405·2, or as TlCl, the atomic weight being then 202·6. Regnault found the specific heat of thallium to be 0·0335, and thus decided the question in favour of the latter view, since $0{\cdot}0335 \times 202{\cdot}6 = 6{\cdot}8$.

A similar instance occurs in the case of indium, the chloride of which contains 38·3 parts by weight of metal to 35·46 parts by weight of chlorine. Indium has a very considerable resemblance to zinc and cadmium, and for this reason the chloride was supposed to have the formula $InCl_2$, giving an

atomic weight of 76·6 to the metal. In 1870 Bunsen[1] ascertained by means of his ice calorimeter that the specific heat of indium is 0·057. Now $0{\cdot}057 \times 76{\cdot}6 = 4{\cdot}4$, or only two-thirds of the atomic heat of the other metals. Hence we must assume that the true atomic weight of the metal is $76{\cdot}6 \times \frac{3}{2} = 114{\cdot}8$. This gives the formula for the chloride, $InCl_3$, which has been confirmed by the vapour density.

The example of uranium may also be quoted. At one time this metal was supposed to have an atomic weight of about 119, and to resemble iron in its chemical characteristics, its oxides being assigned the formulæ UO and U_2O_3. At a later period, however, it was found that the chemical relations of the metal agreed better with the atomic weight 236·7, according to which its oxides would be UO_2 and UO_3. This conclusion was confirmed by Zimmermann, who found its specific heat to be 0·0276, its atomic weight therefore being about 238.[2]

Isomorphism.

15 An account of the general phenomena of isomorphism will be found under "Crystallography." As briefly mentioned in the historical introduction (Vol. I., p. 42), Mitscherlich was the first to perceive that substances which are similar in crystalline form are similar also in chemical composition; he concluded from his observations that the same number of atoms combined in the same way produces the same crystalline form, this latter being independent of the chemical nature of the atoms and depending only on their number and relative position. He pointed out soon afterwards that this relation might be employed for the determination of the relative combining weights of two elements or compounds. Thus, having found that potassium sulphate and potassium selenate, which crystallise in the rhombic system, are isomorphous, he concluded that selenic acid (the anhydride) would, like sulphuric acid, contain three times as much oxygen as the base with which it was combined in the salt in question, this conclusion being afterwards confirmed by analysis.

At the time when Mitscherlich first stated his theory of the relation between atomic composition and crystalline form, the only available means of ascertaining the atomic weights of the metals was that provided by Dulong and Petit's rule,

[1] *Phil. Mag.*, 1871, [4], **41**, 161, 392. [2] *Annalen*, 1885, **232**, 299.

which had been applied only to some thirteen elements. The rule, moreover, had not at that time been extended to the molecular heat of compounds, and hence the atomic weights of a large number of metals could be determined only by analogy, or by arbitrary assumptions. Under these circumstances Mitscherlich's theory of isomorphism proved of great importance, and was at once applied by Berzelius to the determination of the atomic ratios of such elements as chromium, titanium, etc. Thus the ratio of the amounts of oxygen in chromium sesquioxide and chromic anhydride per unit of chromium was known to be 1 : 2, the simplest expression of which, according to the Daltonian system, would be by the formulæ CrO and CrO_2, although Berzelius formulated them for other reasons as CrO_3 and CrO_6. Chromium sesquioxide, however, is isomorphous with ferric oxide, iron being an element the atomic weight of which had been determined by the specific heat method, and hence the formula Cr_2O_3 was given to it. Chromic anhydride thus became CrO_3, which is in full agreement with the fact that the chromates are isomorphous with the sulphates, sulphuric anhydride having been formulated by Berzelius on independent grounds as SO_3.

At present the isomorphous relations of the compounds of an element only supply additional confirmation of the atomic weight, which has now been deduced for every element either from the molecular weight of its compounds, from the atomic heat of the element itself, from the molecular heat of its compounds, or from the ratio of the specific heat of the element at constant pressure to that at constant volume (Vol. I., p. 135).

The elements may be grouped into the following series,[1] the members of which form isomorphous compounds. Elements which form several series of compounds are often found in a corresponding number of isomorphous series, the isomorphous relations of one type of compound being different from those of another.

(1) (*a*) K, Rb, Cs, Tl, (NH_4).
(*b*) Li, Na, Ag.
(2) (*a*) Gl, Mg, Zn, Cd, Mn, Fe, Co, Ni, Os, Ru, Pd, Pt, Cu.
(*b*) Ca, Sr, Ba, Pb, Ra.

[1] Arzruni, *Physikalische Chemie der Krystalle* (Vieweg, 1895). Sonderabdruck aus Graham-Otto's *Ausführliches Lehrbuch der Chemie*, 1 Band, 3 Abtheilung. See also Groth, *Einleitung in die chemische Krystallographie*, pp. 48–53 (Engelmann, Leipzig, 1904), or the English translation of this volume, *Introduction to Chemical Crystallography*, (1906).

(3) La, Di, Yt, Ce, Er.
(4) Al, Fe, Cr, Co, Mn, Ir, Rh, Ga, In, (Ti).
(5) Cu, Hg, Pb, Ag, Au.
(6) Si, Ti, Ge, Zr, Sn, Pb, Th, Mo, Mn, U, Ru, Rh, Ir, Os, Pd, Pt, Fe.
(7) N, P, As, V, Sb, Bi.
(8) Cb, Ta.
(9) S, Se, Cr, Mn, Mo, W, As, Sb, Fe, Te (?).
(10) F, Cl, Br, I, Mn, (CN).

No cases of isomorphism have as yet been observed among the compounds of the following elements:

H, B, Sc, C, and O.

The details of the isomorphous compounds of the metals included in the above series will be found under the several metals.

The Molecular Weights of the Metals.

16 The metals as a rule boil at exceedingly high temperatures, and up to the present it has for this reason been found possible to obtain definite results with the vapour densities of zinc, cadmium, mercury, silver, antimony, bismuth, lead and thallium only.[1] The results obtained indicate that the molecules of these metals are monatomic, although it should be noted that the values obtained for the vapour densities of the four last metals are all somewhat higher than would be expected on that basis. The vapour densities of potassium and sodium have been determined only approximately, since the vapours of these metals attack the material of which the apparatus is constructed. The results, however, point to the conclusion that these two metals form monatomic molecules.

The molecular weights of many of the metals have been determined also by the cryoscopic and vapour-pressure methods of Raoult (Vol. I., pp. 132–5). These experiments render it probable that in nearly all cases the molecules of the metals are identical with their atoms. When tin is used as a solvent for the metals Ni, Ag, Au, Cu, Tl, Na, Pd, Mg, Pb, Zn, Cd, Hg, Bi, and Ca, the solutions which are formed behave on cooling in the same manner as dilute solutions of non-electrolytes in water

[1] Biltz and Meyer, *Zeit. physikal. Chem.*, 1889, **4**, 264; Biltz, *ibid.*, 1896, **19**, 385; Wartenberg, *Ber.*, 1906, **39**, 381; *Zeit. anorg. Chem.*, 1907, **56**, 320.

(*loc. cit.*). Atomic proportions of these metals, when added to a fixed amount of tin, so as to form a dilute solution of the metal, all lower the freezing-point of tin to the same extent. Further, the amount of the depression agrees with that calculated from theoretical considerations, on the assumption that the molecular weights of the dissolved metals are identical with their atomic weights. The numbers obtained for indium and aluminium seem, however, to indicate that the molecules of these metals contain two atoms.[1] The freezing points and vapour pressures of solutions of the metals in mercury have also been examined, and lead to similar conclusions, although the results obtained are not so regular as when tin is the solvent.[2]

17 The identity of atom and molecule has been confirmed in the case of mercury vapour by the determination of the ratio of the specific heat at constant pressure to that at constant volume (see Vol. I., p. 135). In the same way it has been shown that the molecules of sodium and potassium in the state of vapour are monatomic.[3]

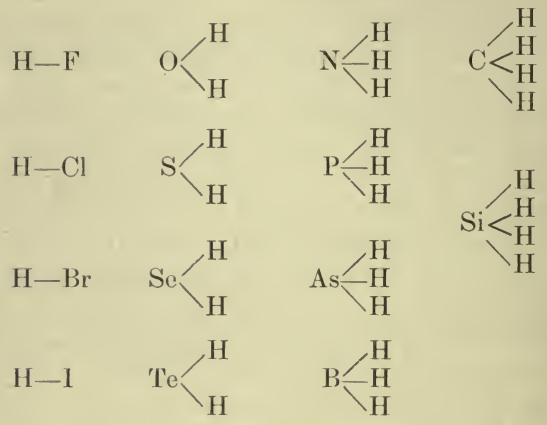
VALENCY OF THE ELEMENTS.

18 In connection with the non-metallic elements it has already been pointed out (Vol. I., p. 145) that the atoms of these elements differ in the number of hydrogen atoms with which they can combine. This varying combining power of the elements is known as *valency* or *quantivalence*, and the elements are described as monovalent, divalent, trivalent, or tetravalent (univalent, bivalent, tervalent, or quadrivalent), or as monads, dyads, triads, or tetrads, according as they combine with one, two, three, or four atoms of hydrogen. This is expressed also by saying that each of these elements has one, two, three, or four *units of affinity* or *bonds*, and in combination with hydrogen each of these is satisfied by combining with the single unit of affinity of the latter. This is graphically expressed in the following formulæ, the mutual bond of affinity being represented by the straight line connecting the two atoms :

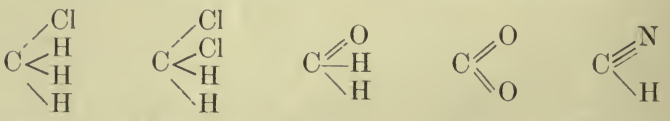
[1] Heycock and Neville, *Journ. Chem. Soc.*, 1890, **57**, 376.

[2] Tammann, *Zeit. physikal. Chem.*, 1889, **3**, 441 ; Ramsay, *Journ Chem. Soc.*, 1889, **55**, 521.

[3] Robitzsch, *Ann. Physik*, 1912, **38**, 1027.



The further investigation of the non-metallic elements has shown that similar relationships are to be found in their compounds with elements other than hydrogen. Thus, in the compounds mentioned above, the hydrogen may be replaced by other elements, and it has been found that those elements which combine with only one atom of hydrogen are able to replace only one atom of that element, whilst the divalent elements are able to replace two atoms, the trivalent three, and so forth. Thus, if we take the compound of carbon and hydrogen, CH_4, we can replace one or more atoms of hydrogen by an equal number of chlorine atoms, two or four atoms by one or two atoms of oxygen, and three atoms by an atom of nitrogen, the graphic formulæ of the compounds obtained being given below :—

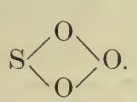


Methyl chloride. Methylene chloride. Form-aldehyde. Carbon dioxide. Hydrocyanic acid

From these and many other similar facts, the conclusion was at first drawn by some chemists that the valency of an element is a constant property, and remains the same in all compounds which it forms. As the number of the compounds whose true molecular weights were ascertained became larger, it was found, however, that this view could not be maintained without modification. Thus phosphorus, which forms the hydride PH_3, yields two chlorides, PCl_3 and PCl_5, and as, in the latter, it is combined with five monovalent atoms, it must in this case be pentavalent,

whilst in PCl_3 and PH_3 it is trivalent. Upholders of the theory of constant valency denied that phosphorus pentachloride was a true compound, and regarded it as a *molecular compound* of PCl_3 and Cl_2, analogous to a salt containing water of crystallisation, basing this view on the fact that when phosphorus pentachloride is volatilised it decomposes into these two portions. It was then shown that by suitable means the pentachloride may be volatilised without decomposition, and that its vapour density then corresponds with the formula PCl_5. Further, a phosphorus pentafluoride has been discovered which is gaseous at the ordinary temperature, and has the molecular formula PF_5. The valency of phosphorus, therefore, towards the halogens cannot be regarded as constant.

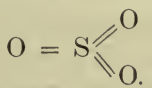
Again, the two chief oxides of sulphur have the formulæ SO_2 and SO_3, and on the assumption that sulphur and oxygen are both divalent the constitutional formulæ were written :—



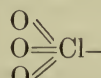
Among the oxygen compounds of chlorine we are acquainted with four oxy-acids having the formulæ $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$, the constitutions of which were represented as follows :—

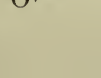
H—O—Cl
H—O—O—Cl
H—O—O—O—Cl
H—O—O—O—O—Cl.

In all these cases, however, another interpretation is possible, namely, that the divalent oxygen is connected directly with the sulphur or chlorine atom, the valency of the latter varying in the different cases, as shown in the following formulæ :—



Cl—O—H
O=Cl—O—H





In such cases, it must be remembered (see Vol. I., p. 147), it is only after the *constitution* of a compound has been ascertained that the valency of the component atoms can be deduced.

No definite proof has hitherto been obtained of the correctness of either view, but the balance of evidence is strongly in favour of the latter, as it is found that those compounds which can be proved to contain oxygen atoms directly combined together in the manner shown in the first series of formulæ, such as hydrogen peroxide, are extremely unstable. It is, moreover, probable that the longer the chain of oxygen atoms, the less would be the stability of the compound, whereas, in reality, the stability of the oxy-acids of chlorine increases with the number of oxygen atoms in the molecule. Sulphur, again, is undoubtedly a hexad in the hexafluoride, SF_6, which is a very stable gas, whilst in the highest compound which has been obtained with chlorine, SCl_4, it is a tetrad. Oxygen, moreover, which is usually a dyad, is probably a tetrad in the salts which many organic oxygen compounds form with acids, and which are termed oxonium salts. It is now, therefore, generally supposed that the valency of an element is not a constant, but a variable, property.

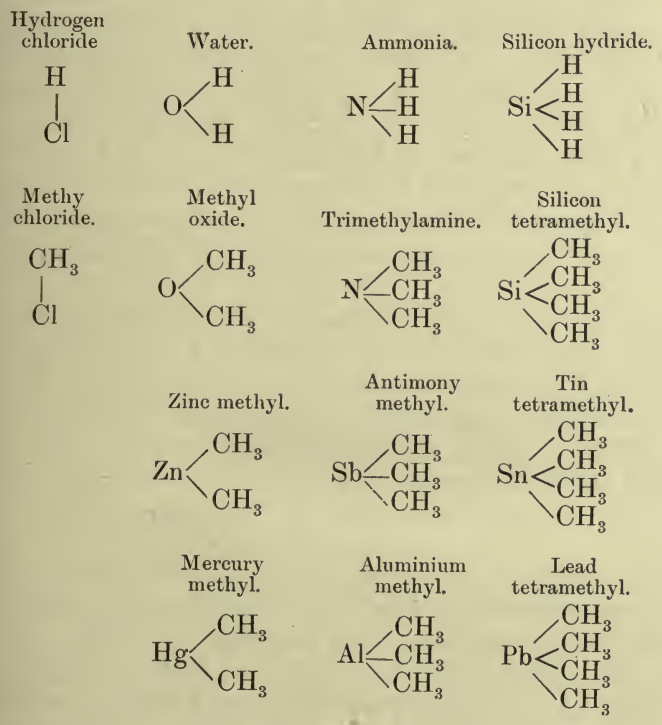
It will, however, be noticed that in the above cases there is a certain regularity in the variation, the valency of an element being always represented by either an odd or even number, and in the great majority of the compounds of the non-metallic elements the same rule holds. Even to this there are a few notable exceptions, such as nitric oxide, NO, in which nitrogen behaves as a dyad instead of as a triad or a pentad, whilst in chlorine peroxide, whose formula has been proved[1] to be ClO_2, chlorine is a tetrad.

19 When we consider the compounds of the metals, it is found that the relations become still more complex than is the case with the non-metals. It is only in recent years that any very definite conclusions could be drawn on this point, as until then the true molecular weights of very few metallic derivatives were known, these having for the most part such high boiling points that the vapour density of very few of them had been determined. The improved methods of determining vapour densities at high temperatures, due chiefly to Victor Meyer and his

[1] Pebal and Schacherl, *Annalen*, 1882, **213**, 113.

pupils,[1] have, however, considerably enlarged the material at our disposal, and the results have necessitated some modification of the older views.

None of the metals combines with hydrogen to form a volatile compound, and hence their valency towards this element cannot be determined. Many metals, however, form volatile compounds with the monovalent alcohol radicals (p. 14). These compounds may be regarded as substituted metallic hydrides, and serve also for the determination of the valency of such metals as form them. The table below gives the constitutional formulæ of some of the compounds of non-metals with hydrogen and alcohol radicals, and of a number of the metallo-organic compounds the vapour densities of which have been ascertained:—



The vapour densities of a number of metallic chlorides, as wel as of a few iodides, have now been determined. The

[1] *Pyrochemische Untersuchungen*, 1884 (Vieweg); and numerous papers, *Ber.*, 1880–1890.

molecular formulæ based on the vapour densities are given below :—

I.	II.	III.	IV.	V.	VI.
$NaCl$	$GlCl_2$	$AlCl_3$	$TiCl_4$	$CbCl_5$	WCl_6
KCl	$CrCl_2$	$CrCl_3$	VCl_4	$TaCl_5$	
KI	$FeCl_2$	$FeCl_3$	$GeCl_4$	$MoCl_5$	
$RbCl$	Cu_2Cl_2	$GaCl_3$	$SnCl_4$	WCl_5	
$CsCl$	$ZnCl_2$	$InCl_3$	$ZrCl_4$		
CsI	$GaCl_2$	$SbCl_3$	UCl_4		
$AgCl$	$SnCl_2$	$BiCl_3$			
$InCl$	$InCl_2$				
$TlCl$	$HgCl_2$				
	$PbCl_2$				

20 A definite conclusion as regards the molecular formula of a compound can be drawn from its vapour density only when the latter remains constant through a considerable range of temperature. In many instances the vapour density diminishes gradually with rise of temperature, and attains a constant value only at temperatures considerably above the boiling point. The same fact has been observed with substances boiling at comparatively low temperatures, such as acetic acid. This appears to indicate the presence in the vapour of a certain proportion of heavier molecules which gradually decompose as the temperature rises. Thus the first determination of the vapour density of ferric chloride, made by V. and C. Meyer,[1] agreed approximately with the formula Fe_2Cl_6. Subsequently, V. Meyer and Grünewald showed [2] that the vapour density of ferric chloride is, even at 448°, rather lower than corresponds to the formula Fe_2Cl_6, and that, as the temperature rises, the density gradually becomes less, until at 750° the value agrees closely with the formula $FeCl_3$, and remains constant up to 1,077°.

At temperatures above 448° a certain amount of the ferric chloride is dissociated into ferrous chloride and chlorine, but at 448° no decomposition of this character takes place, and even here the vapour density is smaller than that required by the formula Fe_2Cl_6; hence, at temperatures not far above the boiling point, a number of the molecules must have a smaller molecular weight than the above, *i.e.*, they must have the formula $FeCl_3$.

Another instance of a similar kind is furnished by aluminium chloride; the older experiments of Deville and Troost in 1857

[1] *Ber.*, 1879, **12**, 1195. [2] *Ber.*, 1888, **21**, 687.

gave the vapour density at 9·3, corresponding to the formula Al_2Cl_6. Nilson and Pettersson,[1] in repeating this determination in 1887 at higher temperatures, obtained the following numbers:—

Temperature.	Vapour density.
440°	7·789
758	4·802
835	4·542
943	4·557
1,177	4·269
1,244	4·247
1,260	4·277

The calculated value for the formula Al_2Cl_6 is 9·2, and for $AlCl_3$, 4·6.

Further examples of this change of density are afforded by stannous chloride and ferrous chloride; in both cases the density at low temperatures is less than that required by the double formulæ Sn_2Cl_4, Fe_2Cl_4, although greater than that needed by the simpler formulæ $SnCl_2$, $FeCl_2$; at higher temperatures, however, constant values corresponding to the simpler formulæ are obtained. Chromic chloride has been likewise proved to have the formula $CrCl_3$, and glucinum chloride to be $GlCl_2$.

The vapour density of cuprous chloride, on the other hand, was found by V. and C. Meyer[2] to correspond to the formula Cu_2Cl_2, both at a bright red heat, and at a white heat. The vapour density of silver chloride has also been determined by Biltz and V. Meyer,[3] and though, as might be expected, the numbers obtained at the high temperature necessary (1,735°) are not very exact, they are sufficient to indicate that the molecular formula is AgCl, and not Ag_2Cl_2.

The conclusion to be drawn from these results is that the chlorides of variable vapour density have the simpler formulæ at high temperatures, but that as the temperature falls combination or association occurs between the molecules. It is not improbable that in many cases the molecules of the fused or solid substance are more complex than those of the gas. This has already been shown experimentally for some liquids (Vol. I.,

[1] *Zeit. physikal. Chem.*, 1887, **1**, 463.

[2] *Ber.*, 1879, **12**, 1283; Biltz and Meyer, *Zeit. anorg. Chem.*, 1897, **15**, 40.

[3] *Zeit. physikal. Chem.*, 1889, **4**, 249.

p. 117), and the extension of the same method to fused salts has led to analogous results.[1]

21 The application to aqueous salt solutions of the methods for ascertaining the molecular weight of substances in solution by the depression of the freezing point and elevation of the boiling point (Vol. I., p. 132) is complicated by the fact that most salts undergo electrolytic dissociation in aqueous solution. The general result obtained, when allowance is made for this by the determination of the electrical conductivity (Vol. I., p. 124), is that in most cases salts have a molecular formula identical with the empirical formula. When salts are dissolved in liquids in which ionisation does not occur, or occurs only to a very small extent, the results obtained point also, as a rule, to the simple formulæ, but in many cases evidence is obtained of molecular association, or combination between two or more molecules, and the results are found to vary with the solvents employed.[2]

The identity of the molecular and empirical formulæ of many chlorides has also been confirmed by the determination, by the vapour pressure method, of their molecular weights when dissolved in boiling bismuth chloride; in this solvent very little electrolytic dissociation occurs, owing to the fact that the chlorine atom is common to both the solvent and the dissolved substance. All the chlorides examined had under these circumstances at 447° the simple formula containing only one atom of metal in the molecule. This holds for the chlorides of Li, Na, K, Rb, Cs, Ca, Ba, Sr, Zn, Cd, Ag, Pb, Mn, and Co, together with ferrous, palladious, and platinous chlorides, and the two chlorides of copper.[3] In all cases where a comparison is possible, these results agree with those deduced from the vapour density at high temperatures, except in the single instance of cuprous chloride.

It appears from the foregoing that in the compounds formed by the metals, the linking together of two atoms of a metal to form a molecule which is stable at a high temperature does not often occur. In certain cases, however, it must be assumed that this sort of combination exists. Tin, for example, forms a volatile compound $Sn_2(C_2H_5)_6$, and Ogg [4] has proved that the

[1] Bottomley, *Journ. Chem., Soc.*, 1903, **83**, 1421; Lorenz and Kaufler, *Ber.*, 1908, **41**, 3727.

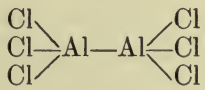
[2] See on this point Werner, *Zeit. anorg. Chem.*, 1897, **15**, 1; Beckmann, *Zeit. physikal. Chem.*, 1903, **46**, 857; Turner, *Journ. Chem. Soc.*, 1911, **99**, 899.

[3] Rügheimer and Rudolfi, *Annalen*, 1905, **339**, 311.

[4] Ogg, *Zeit. physikal. Chem.*, 1898, **27**, 285.

mercurous salts in aqueous solution yield the divalent ion $Hg_2^{\cdot\cdot}$, and not the simple ion $Hg^{\cdot}$, and that they therefore have most probably the double formula Hg_2X_2. In the case of cuprous chloride, the molecule Cu_2Cl_2 certainly exists at 1700°, although in solution in bismuth chloride at 447° only the simple molecules CuCl are present. Moreover, as already stated, the simple molecules capable of existing in the state of gas at high temperatures may form more complex molecules as the temperature falls.

These facts render it difficult to draw definite conclusions as to the valency of the metals in these compounds. Copper in cuprous chloride, for example, must be regarded as monovalent if the formula be CuCl, whilst if the formula be Cu_2Cl_2, it may be looked upon as divalent, the constitution of the chloride being then written Cl . Cu . Cu . Cl. Similarly, aluminium must be regarded as trivalent in its chloride if the molecular formula be $AlCl_3$, whereas it becomes tetravalent if the molecular formula be Al_2Cl_6:



In the present condition of knowledge, it is best to consider the valency of the metals only for the simplest form of each molecule which has been proved to be capable of existence.

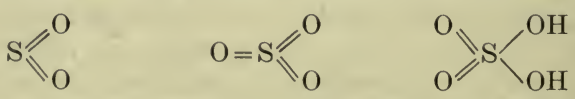
The examination of the list of chlorides (p. 32) shows then not only that the valency of the same metal does vary in different compounds, but that it does not even vary in a regular manner, such as remaining either odd or even. Thus in the case of indium, three volatile chlorides are known, having the formulæ InCl, $InCl_2$, $InCl_3$, in which the metal is a monad, dyad, and triad respectively. Iron is a dyad in ferrous chloride, and a triad in ferric chloride, whilst tungsten acts as a tetrad, a pentad, and a hexad.

In considering the compounds of the metals with oxygen, the available material is not so copious, inasmuch as the actual molecular weights have been determined in but few cases. In most instances the formulæ of the oxides (and of the salts they form with either acid or basic oxides) are taken as the simplest possible, or in some cases as analogous to those of the oxides of elements of the same group whose vapour density has been determined. The valency deduced from these formulæ frequently differs from that obtained from the vapour density

of the chloride of the metal; thus the only volatile chloride of vanadium has the formula VCl_4, whilst in its general deportment this element is analogous to nitrogen and phosphorus, behaving as a triad and pentad. Again, the only volatile chloride of molybdenum has the formula $MoCl_5$, but in many other compounds, such as molybdic acid and the molybdates, the metal acts as a hexad.

22 The valency of an element can no longer, therefore, be regarded as always varying in a regular manner, but appears to vary irregularly according to the nature of the other elements with which it combines. At the same time, an element almost always shows what may be termed a characteristic valency, *i.e.*, a valency which remains constant throughout a large and important series of compounds. Thus, for example, the alkali metals are monovalent in the great majority of their compounds, although a few halogen derivatives have recently been prepared in which they behave as triads and pentads; the metals of the alkaline earths almost always behave as dyads, and nitrogen, phosphorus, and arsenic either as triads or pentads. Carbon in particular shows a very constant tetrad valency, almost the whole of its immense number of compounds containing the element in the tetravalent state. These general regularities find their best expression in the periodic classification of the elements, and will be further considered in discussing the latter.

23 *Werner's Theory of Principal and Supplementary Valencies.* —The molecules formed by the combination of two or more elements are usually not devoid of the power of combining with further atoms or molecules. Thus, for example, sulphur dioxide, SO_2, readily combines with oxygen to form sulphur trioxide, SO_3; this unites with a molecule of water to form sulphuric acid, H_2SO_4, and this again with a further quantity of water to form the crystalline hydrate $H_2SO_4,4H_2O$. According to the ordinary theory of valency, sulphur dioxide is an unsaturated compound in which sulphur acts as a tetrad; in sulphur trioxide the sulphur is a hexad, and the oxygen a dyad:

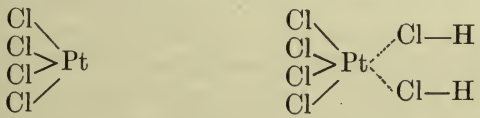


The introduction of water into this molecule can be explained by a rearrangement of the valencies of the elements of the two

compounds, which leads to a constitutional formula for sulphuric acid in accordance with its chemical behaviour. The further introduction of four molecules of water into this molecule cannot be simply represented on the lines of the ordinary theory. It is apparent that some power of combination is still left in such molecules, and this is usually ascribed to the *residual affinity*, either of the molecules as a whole, or of certain of the atoms contained in them.

Very little is known about the mode of combination in such cases, but many theories have been proposed in order to include compounds of this character, among which are to be numbered almost all the double and complex salts of the metals, the ammoniacal metallic compounds, the hydrates, and similar substances.

The most successful attempt in this direction has been made by Werner,[1] whose views are based more especially upon the composition and properties of the ammoniacal metallic derivatives and the complex salts of the metals. According to this theory the atom possesses two kinds of valency, viz., *principal valency*, which is concerned in the combination of atoms or radicals which can exist as ions, or are equivalent to ions; and *supplementary valency*, which is concerned with the combination of radicals which cannot exist as ions. Thus the atoms or groups $-Cl$, $-Na$, $-NO_2$, $-CH_3$, &c., combine by virtue of their principal valencies; groups such as $-OH_2$, $-NH_3$, $-ClK$, $-CrCl_3$, &c., by means of their supplementary valencies. Platinum, for example, combines with four atoms of chlorine by principal valency forming the molecule $PtCl_4$, the highest chloride of platinum which can be obtained. This molecule readily combines, however, with two molecules of hydrogen chloride by the supplementary valencies of the platinum and chlorine atoms, forming chloroplatinic acid, H_2PtCl_6:



The constitution of these molecules is represented above according to Werner's theory, principal valencies being repre-

[1] *Annalen*, 1902, **322**, 261. See also Werner's *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*; an English translation of this volume has been published under the title: "New Ideas on Inorganic Chemistry."

sented by unbroken lines, and supplementary valencies by dotted lines.

The number of atoms which can combine directly with a single atom appears to be to some extent independent of the nature of the particular atoms concerned. The atoms of most elements can unite in this way with six other atoms or groups, which may be regarded as being situated in the primary sphere of action of the central atom, and are said to be *co-ordinated* with it. These six may be united to the central atom either by principal or by supplementary valency, and if any of the principal valencies of this atom remain unsaturated, the radical thus formed has a corresponding power of combining with further atoms, which, however, must remain in the secondary sphere of action of the central atom.

The trivalent atom of cobalt, Co, can, for example, co-ordinate six molecules of ammonia by supplementary valencies, forming a radical $Co(NH_3)_6$, in which the trivalent cobalt atom is still capable of combining with three monovalent atoms of chlorine by principal valency, forming the well-known compound, $[Co(NH_3)_6]Cl_3$, hexammine-cobaltic chloride (luteo-cobalt chloride). In this substance the six molecules of ammonia are regarded as being situated in the primary sphere, and united with the cobalt atom by supplementary valencies, whilst the three chlorine atoms are situated in the secondary sphere of action, and are united with the cobalt by principal valencies.

On the other hand, in the co-ordination radical $[CoCl_3(NH_3)_3]$, both the chlorine atoms and the molecules of ammonia are situated in the primary sphere, the chlorine atoms being united with the cobalt by principal, and the ammonia molecules by supplementary, valency. The trivalent cobalt atom is therefore saturated and incapable of further combination. This substance is known as triammine-cobaltic chloride, and when dissolved in water does not undergo electrolytic dissociation, because the chlorine atoms form part of the complex radical. The solution, therefore, does not yield a precipitate of silver chloride when silver nitrate is added. On the other hand, the hexammine-cobaltic chloride molecule, in which the chlorine is not part of the complex radical, dissociates in aqueous solution into the ions $[Co(NH_3)_6]^{\cdots}$ and $3Cl'$, and the whole of the chlorine is precipitable by silver nitrate.

The maximum number of atoms or groups which can unite directly with a central atom is therefore six, plus the valency

of the central atom. In some cases the co-ordination number is four (carbon, boron, and nitrogen), and it is possibly as high as eight in some instances (molybdenum), but for the great majority of elements it is six.

This theory has proved of great value in the classification of the complex derivatives of the metals, and numerous applications of it will be found under the separate metals. The more recent development of the theory has taken the form of prediction of the existence of isomerides, and the predictions have been verified in a striking manner. The representation of the six co-ordinated groups or atoms as arranged in space round the central atom in the relative positions of the angles of an octahedron, leads to conclusions as to the existence of *cis-* and *trans*-isomerides in certain cases, and of optical isomerides in others. Such isomerides have now been isolated,[1] and this fact gives strong support to Werner's views.

24 *Electrochemical Theory of Valency. Corpuscular Theory of the Constitution of the Atom.*—Concerning the nature of valency very little is at present known. One important relation has, however, been established by the classical researches of Faraday. When a salt of a metal is dissolved in water and the solution is electrolysed, the amount of the metal deposited in a given time depends on the valency which the metal possesses in that salt. Thus when solutions of salts of a univalent and divalent metal, such as the sulphates of silver and zinc, are electrolysed by the same current, two atomic proportions of silver are deposited for each atomic proportion of zinc, the same amount of oxygen being liberated at the anode in each case. Since the same amount of electricity has been conveyed by the ions of the metal in the two cases, it follows that the electrical charge conveyed by each silver ion is only half as great as that conveyed by each ion of zinc. A similar relation is found in other cases, and it may be stated as a general law that the electrical charge which is conveyed by the ion of a metal in the electrolysis of a solution of a salt is directly proportional to the valency of the ion.

These facts have led many chemists to the conclusion that chemical combination is essentially an electrical phenomenon, and occurs always between a positive and a negative radical. This was, indeed, the fundamental principle of the dualistic system of Berzelius, but was rendered truly applicable to the

[1] See Werner, *Ber.*, 1911, **44**, 2449 3231.

facts of chemical combination only by Faraday's discovery of the quantitative laws of electrolysis.[1] This idea is in harmony with the modern view of the structure of the atom, which has been derived largely from the study of the phenomena of the conduction of electricity through gases and solutions, and of radioactivity.

According to this view,[2] an atom of any substance is composed of a large number of corpuscles or electrons, which have a mass of about 1/1000 of that of a hydrogen atom, and carry a negative charge equal to that of a univalent ion in a solution of a salt. These corpuscles are in rapid motion, and are held together by the attraction of an equal positive charge, which may be supposed to be distributed uniformly over the sphere about the centre of which the corpuscles are moving. One or more corpuscles may be detached from the atom, either in consequence of their high velocity, or as a result of the atom colliding with other atoms or free corpuscles. Evidence of this detachment of corpuscles is supplied by the phenomena of the conduction of electricity through gases.

The escape of one corpuscle from an atom will leave the latter with a positive charge, and it will then be more difficult for a second corpuscle to be detached. If stability is reached at this stage, we are dealing with a univalent electropositive atom. It may happen, however, that the positive electrification of the atom resulting from the escape of one corpuscle is not sufficient to prevent the detachment of a second corpuscle. If this should take place, and a condition of stability is then reached, we are dealing with a divalent electropositive atom. Thus atoms which lose one, two, or three corpuscles, acquire positive charges of one, two, or three units.

On the other hand, the corpuscles in an atom may have such small velocities that there is no tendency for them to escape, and such an atom may even be capable of receiving one or more foreign corpuscles without causing the ejectment of any of its own. The magnitude of the negative charge acquired by an atom in this way will depend on the firmness with which the corpuscles are held. If the addition of one foreign corpuscle does not lead to the expulsion of one of the original corpuscles,

[1] See on this point Helmholtz, The Faraday Lecture, *Journ. Chem. Soc.*, 1881, **39**, 277.

[2] Thomson's *Electricity and Matter*, pp. 128–132 (Constable and Co., 1904). See *Phil. Mag*, 1904, **7**, 237; 1906, **11**, 769; also Ramsay, *Journ. Chem. Soc.*, 1908, **93**, 778.

whereas the addition of two foreign corpuscles does so, then the maximum negative charge on the atom would be one unit. According, then, as the number of extra corpuscles which can be so attached is one, two, or three, we are dealing with a univalent, divalent, or trivalent electronegative atom.

From the point of view here described, the valency of an atom depends on the ease with which corpuscles can escape from, or be received by, the atom; this may be influenced to some extent by the environment, and it is therefore intelligible that valency may be affected in some degree by the prevailing physical conditions.

If we imagine a number of atoms which have lost corpuscles mixed with a number of atoms which have retained foreign corpuscles, it is easy to see that the numerical proportion in which the atoms combine in order to form neutral systems must be determined by the relative magnitude of the charges which they carry. In the case of an atom which can neither lose one of its own corpuscles, nor retain a foreign corpuscle, chemical combination would, on this view, be impossible. Such an atom would have the properties of an atom of helium or argon.

This theory is capable of explaining the phenomena of electrolysis, and all reactions which occur between ions, as well as all cases of combination between electropositive and electronegative elements. Considerable difficulties, however, arise when it is applied to elements which are not markedly electropositive or electronegative, and especially to those compounds in which a number of atoms of the same element are combined together. In such a simple compound as ethane, CH_3-CH_3, for instance, it is necessary to suppose that one of the carbon atoms acts as the positive, and the other as the negative element, although no difference between the two has been recognised chemically. Similar considerations hold with regard to the molecules of the elements themselves, many of which are composed of two atoms of the element united together.

Another theory of valency which is electrochemical in character is the one developed by Abegg and Bodländer.[1] According to their view, each element has two kinds of valencies, *normal* and *contra*-valencies, the polarity of which is opposite, and the total number of which is eight. The normal valencies are regarded as the stronger, and correspond with the

[1] *Zeit. anorg. Chem.* 1899, **20**, 453; *ibid.*, 1904, **39**, 330.

commonly accepted valencies of the elements. Thus chlorine possesses one negative normal valency, and seven positive contra-valencies, whilst silver has one positive normal valency and seven (latent) negative contra-valencies. The greater the number of contra-valencies possessed by any particular element the greater is the tendency of this element to form molecular compounds.

Reference should be made here also to Barlow and Pope's theory, according to which the spheres of influence of different atoms are proportional to the fundamental valencies of the atoms. This theory, however, will be discussed at a later stage.

CLASSIFICATION OF THE ELEMENTS.

25 The number of substances at present described as elementary is about 80 (see this vol., p. 2), and of these about 70 have been subjected to close investigation, and their properties and those of their compounds definitely ascertained. Their atomic weights have also been determined with a moderate degree of accuracy, and it has been shown that these numbers really represent atomic weights, and not simply the equivalents of the elements (see pp. 14–27).

The question naturally arises whether these substances are in reality incapable of further decomposition, or whether by suitable means they might not in turn be resolved into still simpler substances. Indeed, very soon after the enunciation of Dalton's atomic theory, speculations as to the compound nature of the so-called elements were published. Thus, in the year 1815, Prout suggested [1] that the elements were in reality all composed of hydrogen, basing his supposition on the numbers at that time adopted for the atomic weights compared with hydrogen, which were in most cases whole numbers. The extreme simplicity of the hypothesis attracted many adherents, but the later careful determination of the atomic weights by Berzelius did not confirm it. It was somewhat modified by Dumas,[2] who assumed that the unit weight of hydrogen was itself composed of two or even four atoms, in which case the atomic weights would all be multiples of either 0·5 or 0·25.

[1] Anonymously published in Thomson's *Annals of Philosophy*, 1815, vol. vi., "On the Relations between the Specific Gravities of Bodies in their Gaseous State and the Weight of their Atoms."

[2] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.

The very careful experiments of Marignac, and especially of Stas (p. 12), which were carried out with extraordinary care for the purpose of testing Dumas's hypothesis, showed that the atomic weights of many elements are multiples neither of 1, nor of 0·5, nor of 0·25, and this conclusion has been confirmed by more recent investigations. At the same time, it is worth while noting that of the 83 elements in the atomic weight table no fewer than 43 have atomic weights within one-tenth of a unit above or below an integral number. It appears that the probability against such a condition being fortuitous is 20,000 millions to one.[1]

Although Prout's hypothesis has not been confirmed, the inquiries made to investigate its validity brought to light a number of relationships which exist between the atomic weights of analogous elements. Even before the enunciation of the atomic theory, and before the true nature of the alkalis and alkaline earths was known, Richter[2] had pointed out that those quantities of the alkaline earths which neutralise a given weight of an acid, could be arranged as members of the arithmetical progression $a+nb$, in which the value of n was 0 for alumina, 1 for magnesia, 3 for lime, 9 for strontia, and 19 for baryta. In 1817 Döbereiner called attention to the fact that the atomic weight of strontium is the mean of those of the two closely allied elements calcium and barium, and later on the same was found to be approximately true in the case of other groups of three elements, or *triads*, as they were called. In 1850 Pettenkofer[3] brought forward the view that, in the case of analogous elements, the difference in the atomic weights is either a constant or a simple multiple of that constant; thus, using the whole number nearest to the atomic weight, the following series were given:

		Difference.			Difference.
Li	= 7		O	= 16	
		16			16
Na	= 23		S	= 32	
		16			3 × 16
K	= 39		Se	= 80	
					3 × 16
			Te	= 128	

[1] See Ramsay, B.A. Reports, 1911, 10.

[2] *Ueber die neuern Gegenstände der Chymie*, 1797, **8**, 21.

[3] *Münchene Gelehrten Anzeigen*, 1850, **30**, 261; quoted in *Annalen*, 1858, **105**, 187.

This idea was further developed by Kremers, Gladstone, and especially by Dumas, and attention was drawn to the analogy existing between such a group of elements and the homologous hydrocarbon radicals. Thus, if we take the radicals of the C_nH_{2n+1} and C_nH_{2n} series, we have:

	Difference.		Difference.
$CH_3 = 15$		$C_2H_4 = 28$	
	14		14
$C_2H_5 = 29$		$C_3H_6 = 42$	
	14		14
$C_3H_7 = 43$		$C_4H_8 = 56$	

When the more exact modern numbers are employed, it is found that the differences between the atomic weights of the elements are not quite so regular as when the above approximate numbers are taken, but even then the approximation to Pettenkofer's rule seems far too close to be due to chance. Further investigation showed that a very large number of the elements could be divided into groups showing similar relationships, and, in 1864, Lothar Meyer[1] tabulated a large number of such groups, and arranged a certain number of the elements in the order given in the table on p. 45, according in the first place to the magnitude of their atomic weights, and in the second place to their valency.

Natural Arrangement of the Elements.

26 The discovery of any system which should embrace the whole of the elements was rendered possible only by the adoption of the consistent atomic weights proposed by Cannizzaro in 1858. Previous to this date, the attempts at classification consisted only in the division of the elements into groups, and did not bring out the relations which exist between them as a whole. This was first achieved in what is usually known as the *natural arrangement of the elements.*

The first attempt at such an arrangement was made by de Chancourtois[2] in 1862, in whose system the elements were arranged in order of their atomic weights along a spiral line drawn round a vertical cylinder, the surface of which was

[1] *Die modernen Theorien der Chemie*, 1864, 1st edition, p. 137.

[2] *Compt. rend.*, 1862, **54**, 757, 840, 967; 1862, **55**, 600: 1863, **56**, 263, 479; 1866, **63**, 24; see also Hartog, "A First Foreshadowing of the Periodic Law," *Nature*, 1892, **41**, 186.

——	rad.	Triad.	Dyad.	Monad.	Monad.	Dyad.
	—	—	—	—	Li = 7·03	(Gl = 9·3 ?)
Difference =	—	—	—	—	16·02	14·7
	C = 12·0	N = 14·04	O = 16·00	F = 19·0	Na = 23·05	Mg = 24·0
Difference =	16·5	16·96	16·07	16·46	16·08	16·0
	Si = 28·5	P = 31·0	S = 32·07	Cl = 35·46	K = 39·13	Ca = 40·0
Difference =	$\frac{89·1}{2}$ = 44·55	44·0	46·7	44·51	46·3	47·6
	—	As = 75·0	Se = 78·8	Br = 79·97	Rb = 85·4	Sr = 87·6
Difference =	$\frac{89·1}{2}$ = 44·55	45·6	49·5	46·8	47·6	49·5
	Sn = 117·6	Sb = 120·6	Te = 128·3	I = 126·8	Cs = 133·0	Ba = 137·1
Difference =	89·4 = 2 × 44·7	87·4 = 2 × 43·7	—	—	71 = 2 × 35·5	—
	Pb = 207	Bi = 208	—	—	(Tl = 204 ?)	—

divided into sixteen vertical strips by straight lines. The points occupied by the various elements on this surface were termed "characteristic points," or "geometrical characters." De Chancourtois enunciated the fundamental theorem of his system as follows:—"The relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points. For instance, oxygen, sulphur, selenium, tellurium, and bismuth,[1] fall approximately on the same vertical generating line, while magnesium, calcium, iron, strontium, uranium, and barium fall on the opposite generating line. On either side of the first of these lines we find hydrogen and zinc on the one hand, bromine, iodine, copper, and lead on the other; parallel to the second line we find lithium, sodium, potassium, manganese, &c."

On Fig. 1, p. 47, will be found the representation of the first two turns of de Chancourtois' helix, the surface of the cylinder being developed on the plane surface of the paper, and it will be seen that the elements which lie on the same generating line do belong to the same family.

27 Very shortly afterwards (1864) several similar attempts at a classification of the elements as a whole were made independently by Newlands,[2] who arranged the elements in order of their atomic weights, and finally placed them in seven horizontal series, each consisting of eight members, as shown in the following table:

H	F	Cl	Co, Ni	Br	Pd	I	Pt
Li	Na	K	Cu	Rb	Ag	Cs	Os
Gl	Mg	Ca	Zn	Sr	Cd	Ba	Hg
B	Al	Cr	Yt	Ce	U	Ta	Tl
C	Si	Ti	In	Zr	Sn	W	Pb
N	P	Mn	As	Di	Sb	Cb	Bi
O	S	Fe	Se	Rh, Ru	Te	Au	Th

According to Newlands, the properties of an element in any vertical group are analogous to those of the elements in the corresponding position in the other groups. From analogy with the musical notes, he gave to this relationship the name of the "Law of Octaves."

Both of these proposals, however, received very little attention

[1] Probably a misprint, as bismuth does not fall on the same line in the table.

[2] *Chem. News*, 1864, **10**, 59, 94; 1865, **12**, 83, 94; 1866, **13**, 113, 130. See also Newlands, *On the Discovery of the Periodic Law*, 1884. (E. and F. N. Spon.)

from chemists; indeed, they seem to have been almost entirely forgotten. In fact, a systematic arrangement of the

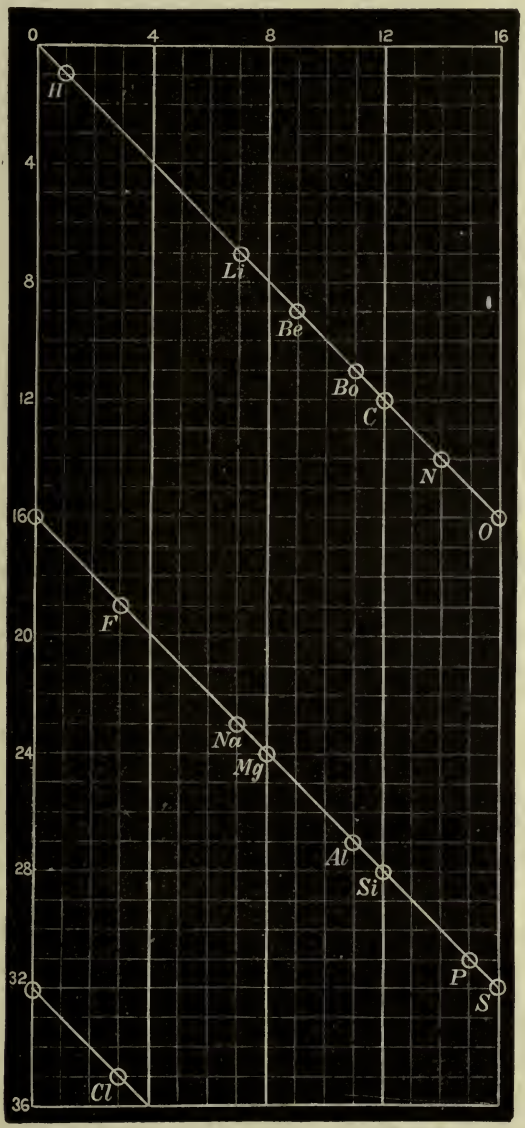


Fig. 1.

elements according to their atomic weights appeared to some chemists almost as absurd and unnatural as an alphabetical arrangement. In the year 1869, however, the same system of

classification, but on a wider basis, was proposed by the Russian chemist Mendeléeff,[1] without any previous knowledge of the work of the above-named chemists. His classification not only included the elements then known, but also left room for many elements at that time undiscovered. He showed that when the elements are arranged in the order of their atomic weights, they may be divided into groups, in each of which a similar gradation of properties from element to element occurs, the properties of the elements thus appearing as periodic functions of the atomic weight.

At a slightly later date, Lothar Meyer,[2] continuing his investigation of the relations between the elements, which had already led to the publication of the table given on p 45, independently put forward views which were almost identical with those of the Russian chemist, and it is to these two investigators that the chief developments of the natural classification of the elements are due.

The Periodic System.

28 In his original paper,[3] Mendeléeff sums up his conclusions as follows:

(1). The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

(2). Elements which are similar as regards their chemical properties have atomic weights which either have nearly the same value (*e.g.* platinum, iridium, osmium), or increase regularly (*e.g.* potassium, rubidium, cæsium).

(3). The arrangement of the elements, or of groups of elements, in the order of their atomic weights corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent, among other series, in that of lithium, glucinum, boron, carbon, nitrogen, oxygen, and fluorine.[4]

(4). The elements which are most widely diffused have *small* atomic weights.

(5). The *magnitude* of the atomic weight determines the

[1] *Zeitschr. Chem.*, 1869, 405; *Annalen*, Suppl., 1872, **8**, 133.

[2] *Annalen*, Suppl., 1870, **7**, 354.

[3] *J. Russ. Phys. Chem. Soc.*, 1869, **1**; quoted in Faraday Lecture, *Journ. Chem. Soc.*, 1889, **55**, 634.

[4] Barium and iron are printed by mistake in the English original (*loc. cit.*) instead of boron and fluorine.

character of the element just as the magnitude of the molecule determines the character of a compound body.

(6). We must expect the discovery of many yet *unknown* elements, *e.g.* elements analogous to aluminium and silicon, the atomic weights of which would be between 65 and 75.

(7). The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

(8). Certain characteristic properties of the elements can be foretold from their atomic weights.

In the table given on pp. 50–51 the elements are arranged according to the system of Mendeléeff and Lothar Meyer, with the addition of a group numbered zero, containing the helium family of elements,[1] and it will be seen that they fall into nine groups, each group occupying one of the vertical columns in the table, whilst there are twelve horizontal series or periods. The members of each group show in most cases a close connection with each other, which is most noticeable in the case of elements belonging to alternate horizontal series. In the table, therefore, the elements in each group are arranged on alternate sides of the column, each group becoming thus divided into two sub-groups, the members of one of which are situated in the *even* horizontal series, whilst the others fall in the *odd* series. Thus in the second group we have the two sub-groups, Gl, Ca, Sr, Ba, Ra, situated in the even horizontal series, and Mg, Zn, Cd, Hg, in the odd. The eighth group is somewhat anomalous, as it appears to occur only in the even periods or series, and, unlike the other groups, always contains three members, the atomic weights of which are more nearly equal than is usually the case.

An inspection of the table shows that the first group contains all the alkali metals, the second group those of the alkaline earths, and also the metals glucinum, magnesium, zinc, cadmium, and mercury. In the third group we find the family, aluminium, gallium, and indium; in the fourth, carbon, silicon, titanium, zirconium, and tin; in the fifth, nitrogen, phosphorus, vanadium, arsenic, antimony, and bismuth; in the sixth, oxygen, sulphur, selenium, and tellurium; and in the seventh, the halogens. The eighth group includes, in addition to the closely

[1] Ramsay, *Ber.*, 1898, **31**, 3111; Mendeléeff *Principles of Chemistry* (1905), vol. ii. p. 20.

Group.	0.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
					MH_4	MH_3	MH_2	MH	Volatile Hydrogen compounds.
Series 1		H 1·008							
„ 2	He 3·99	Li 6·94	Gl 9·1	B 11·0	C 12·00	N 14·01	O 16·00	F 19·0	
„ 3	Ne 20·2	Na 23·00	Mg 24·32	Al 27·1	Si 28·3	P 31·04	S 32·07	Cl 35·46	
„ 4	A 39·88	K 39·10	Ca 40·07	Sc 44·1	Ti 48·1	V 51·0	Cr 52·0	Mn 54·93	Fe 55·84 Co 58·97 Ni 58·68
„ 5		Cu 63·57	Zn 65·37	Ga 69·9	Ge 72·5	As 74·96	Se 79·2	Br 79·92	
„ 6	Kr 82·92	Rb 85·45	Sr 87·63	Yt 89·0	Zr 90·6	Cb 93·5	Mo 96·0	—	Ru 101·7 Rh 102·9 Pd 106·7

„	7		Ag 107·88	Cd 112·4	In 114·8	Sn 119·0	Sb 120·2	Te 127·5	I 126·92		
„	8	Xe 130·2	Cs 132·81	Ba 137·37	La 139·0	Ce 140·25	—	—	—	—	— —
„	9		—	—	—	—	—	—	—		
„	10	—	—	—	—	—	Ta 181·5	W 184·0	—	Os 190·9	Ir 193·1 Pt 195·2
„	11		Au 197·2	Hg 200·6	Tl 204·0	Pb 207·10	Bi 208·0	—	—		
„	12	Nt 222·4	—	Ra 226·4	—	Th 232·4	—	U 238·5	—	—	— —
			M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_4	Highest salt-forming oxides.

allied metals, iron, cobalt, and nickel, the whole of the elements known as the platinum metals. In almost all of these cases, the elements mentioned had been classed as members of the same family before Mendeléeff's work was published, and their continued occurrence in the same group is strong evidence in favour of the general correctness of his views.

Cases will be observed, however, in which there is no very evident connection between members of the two sub-groups comprised in the same group, as for example in the case of silver, copper, and gold on the one hand, and the alkali metals on the other, in the first group; a considerable number of resemblances can indeed be traced, but these are not so prominent as to have led previously to these elements being classified together. In the sixth group also there is very little obvious connection between chromium, molybdenum, and tungsten on the one hand, and the elements of the sulphur group on the other, nor in the seventh group between manganese and the halogens. It will, however, be noticed that in all these cases the elements in question come either just before or just after the occurrence of the eighth group, and it is probable that their somewhat peculiar relationship is connected with the existence of this group.

Mendeléeff suggested an alternative method of tabulation which overcomes certain of these difficulties, and, with some modifications and additions, this is given on page 53. The elements forming series 2 and 3 (pp. 50–51), *i.e.* those which have the lowest atomic weights, and which differ in many respects from the members of the same groups having higher atomic weights, are regarded as typical elements, and the remainder are arranged in double periods, each consisting of an odd and even series of the first table. The two sub-groups into which each group in the table pp. 50–51 is divided are thus separated, the even series coming at the commencement of the long period, the odd series at the end, and the elements of group VIII in the centre.

The typical elements are probably best regarded as being common to both the sub-divisions of the group to which they belong. Thus Li and Na are common to the sub-groups headed by K and Cu; Gl and Mg to those headed by Ca and Zn, &c.[1]

[1] A table in which these relations are very clearly demonstrated has been published by Orme Masson, *The Classification of the Chemical Elements* (Neville, Mullen and Slade, London and Melbourne). See also Richards, *Amer. Chem. J.*, 1898, **20**, 543.

Natural Arrangement of the Elements. Second Table.

									H
(1)	He	Li	Gl	B	C	N	O	F	} Typical Periods.
(2)	Ne	Na	Mg	Al	Si	P	S	Cl	

																		} Double Periods.
(3)	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
(4)	Kr	Rb	Sr	Yt	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
(5)	Xe	Cs	Ba	La	(Ce?)	—	—	—	—	—	—	—	—	—	—	—	—	—
(6)	—	—	—	—	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
(7)	Nt	—	Ra	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—

Even series in table, pp. 50–51. Eighth group in table, pp. 50–51. Odd series in table, pp. 50–51.

At either end of the typical series its members are much more closely related to one of the sub-groups than to the other, whilst towards the middle of the series this difference is not so striking. Thus Li and Na are more analogous to K, Rb, and Cs (even series, pp. 50–51) than to Cu, Ag, and Au ; F and Cl, on the other hand, are more closely related to Br and I (odd series, pp. 50–51) than to Mn, whilst C and Si show considerable analogy both to Ti and Ge.[1]

A comparison of the first two double periods (Nos. 3 and 4 in the table, p. 53), which contain only one space to be filled by a missing element, shows the very complete analogy which exists between them. In the later double periods so many elements are at present missing that the relations are not so apparent, although in numerous cases they are still distinctly seen. This arrangement, moreover, corresponds more closely with the periodic variation in the physical properties of the elements (p. 57).

As the atomic weight becomes higher, the change of properties in passing from any element to the one with the next higher atomic weight becomes less marked, and among those having the highest atomic weights, considerable resemblance is frequently noticed between two successive elements. Thus gold in many properties resembles both platinum and mercury, and lead is nearly related to thallium on the one hand, and bismuth on the other.

Chemical Properties in Relation to the Periodic System.

29 The periodic variation of both physical and chemical properties as we pass from group to group must now be considered, taking first the chemical properties.

Group O is occupied by the monatomic gases of the helium family, which form no compounds.

The most strongly electropositive elements known, whose oxides act almost exclusively as bases, or at most as neutral substances, occur in groups I and II (table, pp. 50–51), whilst the strongly electronegative elements, whose chief oxides form strong acids, occur in the sixth and seventh groups. The third, fourth, and fifth groups occupy an intermediate position,

[1] Abegg, *Ber.*, 1905, **38**, 1386.

the members of the third group yielding oxides which, with the exception of those of the elements having the lowest atomic weights, have for the most part basic properties, but frequently act as acids towards stronger bases; in the fourth and fifth groups the acidic nature of the oxides is most prominent in the case of members of lower atomic weight, whilst the higher members show an increasing tendency to form basic oxides. Those members of the sixth and seventh groups which fall towards the centre of the double periods form both basic and acidic oxides, the acid-forming oxides being those containing the most oxygen, and generally corresponding in formula with the acid-forming oxides of the other elements of the same vertical group. The members of the eighth group usually form basic oxides, but the higher oxides of ruthenium and osmium are strong acid-forming oxides.

Considering the arrangements in short and long periods (p. 53), it is seen that the elements of the helium group, which must be regarded as electrochemically indifferent, fall between the strongly electronegative halogens and the strongly electropositive alkali metals. Towards the centre of the long periods on the other hand, a more gradual change in chemical properties occurs, through the medium of the metals of group VIII.

It is a remarkable fact that, excluding the first two series, only the elements of the odd series (pp. 50–51) form organometallic derivatives of the type M_xR_y, in which M is a metal and R a hydrocarbon radical. The composition of these compounds corresponds with that of the volatile hydrogen compound formed by the typical elements of the group. Thus the compounds $Zn(C_2H_5)_2$, $Sn(C_2H_5)_4$, and $Sb(C_2H_5)_3$ are known, whilst no such substances have been obtained from calcium, titanium, or vanadium.

Valency.

30 It has already been stated that the valency of an element cannot be regarded as constant, but that it varies according to the nature of the elements with which combination occurs. There is nevertheless, in general, a regularity in the valency of the elements in the majority of their compounds, and we usually speak of them as monovalent, divalent, &c., according to their behaviour in the most characteristic of their compounds

This typical valency shows in a marked manner a periodic variation with the atomic weight.

The group numbered zero contains the remarkable monatomic elements of the helium group, which, so far as is at present known, form no compounds whatever, and must therefore be presumed to have zero valency. Group I contains the whole of the metals which are usually monovalent towards hydrogen, the halogens, and the alkyl radicals, and also to oxygen, the typical formulæ of the compounds being $M^{I}R$ ($R = H, CH_3, Cl$, &c.) and $M_2^{I}O$. The metals of the second group act in most cases as divalent elements towards the halogens and alkyl radicals, and also to oxygen, the typical formulæ being $M^{II}R_2$ and $M^{II}O$. In the third group we find the elements which are usually trivalent in their compounds both with hydrogen, or other monovalent radicals, and with oxygen, the typical formulæ of these being $M^{III}R_3$ and $M_2^{III}O_3$. In the fourth, we have the general formulæ $M^{IV}R_4$ and $M^{IV}O_2$, but, in addition, compounds are formed by these elements having the same general formula as those of Group II. In all these cases it is found that among the members having the highest atomic weights the regularity is less marked; thus gold is more frequently trivalent than monovalent, thallium forms compounds in which the metal is monovalent, and lead in its most characteristic compounds is divalent.

Passing on to the fifth group, it is found that the characteristic valency in the hydrogen compounds differs from that in the oxygen compounds, the members being trivalent in the hydrides, and pentavalent in the highest oxides, the general formulæ being $M^{III}H_3$ and $M_2^{V}O_5$. They also form characteristic compounds with oxygen in which the metal is trivalent, and behave towards the halogens in the same manner as towards oxygen. In the sixth group the characteristic valency again becomes less towards hydrogen, the typical formula being $M^{II}H_2$, whilst with oxygen they form the characteristic acid-forming oxides $M^{VI}O_3$, and with halogens the compounds $M^{VI}Cl_6$. With oxygen and halogens they form, in addition, compounds having the same general formulæ as those of the elements of Groups II and IV. The members of the seventh group are, like those of the first, monovalent towards hydrogen, but they are heptavalent towards oxygen in their highest oxides, which have the general formula $M_2^{VII}O_7$. Many of them also form oxides corresponding to those of the first, third, and fifth groups.

In the eighth group no very characteristic valency is noticeable, but it is only in this group that oxygen compounds containing an octavalent element are found; only two of these are at present known, namely RuO_4 and OsO_4. A characteristic of many members of this group is the formation of stable complex cyanides, such as the ferrocyanides, in which the metal is contained in the acid radical, and also of the remarkable series of compounds derived from ammonia, such as the cobaltammonium and platinammonium salts.

Physical Properties of the Elements in Relation to the Periodic System.

31 As with the chemical properties, so it is found that almost all the physical properties of the elements are periodic functions of the atomic weight.

(1) Specific Gravity and Atomic Volume.

One of the most characteristic properties of the elements is their specific gravity in the solid or liquid state, which has been determined with considerable accuracy in the majority of cases. The following table (Landolt and Börnstein, 1912) gives the most reliable determinations of the specific gravity at the ordinary temperature (water = 1).

Specific Gravity of the Elements.

Aluminium . . .	2·70	Chromium . . .	6·7
Antimony . . .	6·62	Cobalt	8·6
Arsenic	5·72	Columbium . . .	8·4
Barium	3·8	Copper	8·93
Bismuth . . .	9·80	Gallium	5·92
Boron	2·45	Germanium . . .	5·46
Bromine (liquid) .	3·14	Glucinum . . .	1·93
Cadmium . . .	8·64	Gold	19·2 –19·4
Cæsium	1·88	Indium	7·2
Calcium	1·55	Iodine	4·94
Carbon (amorphous)	1·7 – 1·9	Iridium	22·4
„ (graphite).	2·1 – 2·3	Iron	7·86
„ (diamond).	3·5 – 3·6	Lanthanum . . .	6·15
Cerium	6·8	Lead	11·34
Chlorine (liquefied)	1·44	Lithium	0·53

SPECIFIC GRAVITY OF THE ELEMENTS (*continued*).

Magnesium	1·74	Selenium	4·3 – 4·8
Manganese	7·39	Silicon	2·0 – 2·5
Mercury (liquid)	13·55	Silver	10·42–10·53
Molybdenum	9·0	Sodium	0·97
Neodymium	6·96	Strontium	2·54
Nickel	8·8	Sulphur	1·92– 2·07
Osmium	22·48	Tantalum	16·6
Palladium	11·5	Tellurium	6·25
Phosphorus (yellow)	1·83	Thallium	11·85
„ (red)	2·20	Thorium	11·0
Platinum	21·4	Tin	7·28
Potassium	0·86	Titanium	4·5
Praseodymium	6·47	Tungsten	19·1
Rhodium	12·1	Uranium	18·7
Rubidium	1·52	Vanadium	5·5
Ruthenium	12·26	Zinc	6·86– 7·2
Samarium	7·75	Zirconium	6·4

The following are the densities (water = 1), at their boiling points, of elements which are gaseous under atmospheric conditions :—

Argon	1·405	Krypton	2·155
Chlorine	1·56	Nitrogen	0·81
Fluorine	1·14	Oxygen	1·118
Helium	0·12	Xenon	3·52
Hydrogen	0·07		

The specific gravity of a given element often varies slightly not only with the temperature, but also with the physical condition. Thus cast metals, or metals deposited electrolytically, become denser when rolled and hammered, electrolytic copper having a sp. gr. of 8·952, which rises to 8·958 when rolled, and cast zinc a sp. gr. of 7·0, whilst that of rolled zinc is 7·2. The different allotropic modifications of the same element also have as a rule different specific gravities, but in all these cases the difference is usually small compared with the differences between the numbers for the different elements.

The periodic variation of the specific gravity at once becomes manifest if the numbers are placed under the symbols of the

elements in the periodic table. Thus, taking the second typical period and first double period, we have the following:—

	Na	Mg	Al	Si	P	S	Cl
Sp. gr.	0·97	1·74	2·70	2·5	2·0	1·9	1·4

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
0·86	1·6	—	4·5	5·5	6·7	7·4	7·9	8·6	8·8

	Cu	Zn	Ga	Ge	As	Se	Br
	8·9	7·0	5·9	5·5	5·7	4·4	3·1

The specific gravity is low at the beginning of both periods, increases regularly to a maximum in the middle, and then decreases until it has again become very low at the end of the periods. It has already been noted that the difference between the atomic weights of the successive elements forming the centre of the double period is smaller than the average, and it will be observed that the variation of specific gravity also is less for these elements.

32 These relations become more strongly marked if, instead of the specific gravities, we take the atomic volumes, *i.e.* the numbers of cubic centimetres which would be occupied by the atomic weights of the elements in grams. If these are arranged, as suggested by Lothar Meyer, so that the ordinates represent the atomic volumes, and the abscissæ the atomic weights, and the points denoting the atomic volumes are then joined, we obtain a line[1] which exhibits the periodic relations in a graphic manner.

This diagram is shown on p. 60, up to and including barium: after this metal the number of gaps due to incompletely investigated or missing elements becomes so large that the diagram is very incomplete, and this portion has therefore been omitted.

It will be seen that the atomic volume reaches a maximum at

[1] Mendeléeff points out that this diagram is open to the objection that it does not indicate that there is only a limited and definite number of elements in each period, but might be taken to imply that any number of elements might occur in each period; thus, for example, it might be assumed that an element of atomic weight 25 might exist between Mg and Al, whose atomic volume would then be about 13, and whose properties would be intermediate between those of the two metals named; for such an inference there is in reality no ground, and it must therefore be borne in mind that the line joining the points representing the atomic volumes is not a true curve, such as, for example, those representing the solubilities of salts, but is simply drawn to render the periodic variation more evident to the eye.

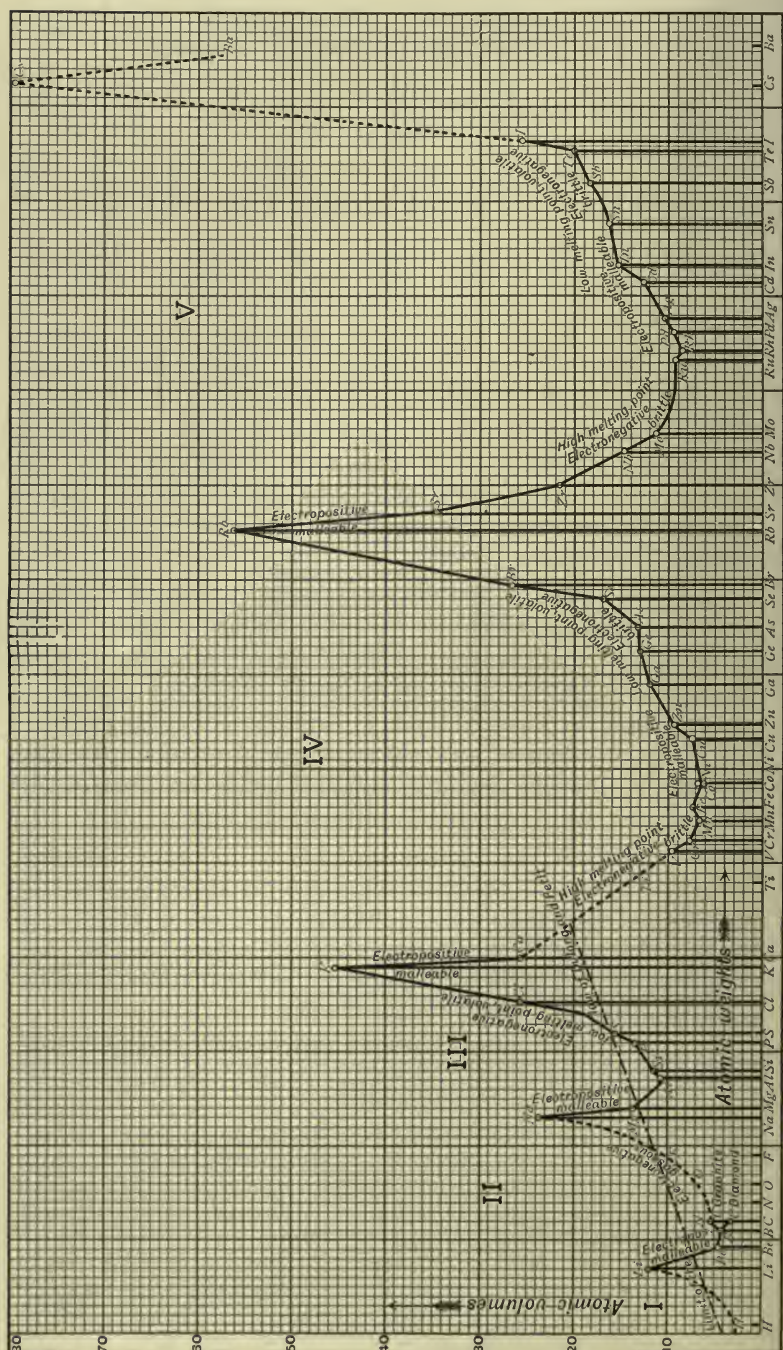


FIG. 2.—Lothar Meyer's Atomic Volume Diagram.

the commencement of each of the two typical periods, and then at the commencement of the double periods, falling to a minimum at the middle and then again rising to the end of the period, and from the last member of each period a further rise is observed to the initial member of the next. This diagram, moreover, brings out relationships which are not otherwise so readily perceived. Thus elements whose atomic volumes are very nearly equal possess very different properties according as they are on an ascending or a descending portion of the line or, in other words, according as they have a smaller or larger atomic volume than the element having the next higher atomic weight. This is exemplified in the cases of aluminium and phosphorus, chlorine and calcium, molybdenum and cadmium, &c. Elements which are characterised by the properties of ductility or brittleness always occur in corresponding positions in the diagram, the ductile elements being found at a maximum or minimum, or immediately following the latter. The periodic variation in these properties is clearly indicated in the diagram.

The work of Richards[1] has shown that the line representing the variation of compressibility of the solid elements with their atomic weight runs parallel to the atomic volume line, and this suggests that atomic volume and compressibility are fundamentally connected. According to Richards' theory of compressible atoms, this connection is a natural one, for it is to be expected that the atoms with a large volume should be more compressible than those which have a small volume and are therefore presumably under great cohesive pressure.

(2) Melting Point of the Elements.

33 Another characteristic property of most elementary substances is the melting point, although this has not been accurately determined in the case of so many elements as the specific gravity, chiefly owing to the difficulties of obtaining correct results for those elements which melt either at a very high or a very low temperature. The following list gives the melting points and boiling points of the elements, so far as definite values are available (Landolt and Börnstein).[2]

[1] See *Journ. Chem. Soc.*, 1911, **99**, 1214.

[2] See also Harker, *Proc. Roy. Institution*, 1912.

Melting and Boiling Points of the Elements.

	Melting point.	Boiling point.
Helium	—	−268·7° C.
Hydrogen	−258·9° C.	−252·6
Oxygen	−227	−182·5
Fluorine	−233	−187
Nitrogen	−210·5	−195·5
Argon	−187·9	−186·1
Krypton	−169	−151·7
Xenon	−140	−109·1
Chlorine	−101·5	− 33·7
Mercury	− 38·8	357
Bromine	− 7·3	58·6–63·0
Cæsium	26·5	670
Gallium	30·1	—
Rubidium	38·5	696
Phosphorus	44·3	287·3
Potassium	62·5	757·5
Sodium	97·6	877·5
Iodine	113·0	184·3
Sulphur	112·8 119·2	444·6
Indium	155	—
Lithium	179	—
Selenium	217	690
Tin	231·9	ca. 2270
Bismuth	270	1420–1435
Thallium	303	—
Cadmium	321	778
Lead	327	1525–1580
Zinc	419	918
Tellurium	455	1390
Cerium	623	—
Antimony	630	ca 1440
Magnesium	650	ca 1120
Aluminium	657	ca 1800
Calcium	800	—
Strontium	ca 800	—
Lanthanum	810	—
Neodymium	840	—
Barium	850	—

MELTING AND BOILING POINTS OF THE ELEMENTS.
(*continued*).

	Melting point.	Boiling point.
Praseodymium	940° C.	—
Germanium	ca 958	—
Silver	961	ca 2000° C.
Gold	1064	—
Copper	1083	—
Manganese	ca 1240	ca 1900
Nickel	1452	—
Cobalt	1490	—
Iron	ca 1520	ca 2450
Palladium	1549	—
Chromium	ca 1550	ca 2200
Vanadium	ca 1680	—
Platinum	1750	—
Columbium (Niobium)	ca 1950	—
Molybdenum	ca 2110	—
Tantalum	ca 2250	—
Iridium	ca 2300	—

The boiling points of certain metals have also been determined in a high vacuum by Krafft,[1] with the following results:—

Mercury	155° C.	Zinc	550° C.
Potassium	365	Bismuth	993
Sodium	418	Silver	1360
Cadmium	450		

It has, moreover, been shown by Moissan[2] that all the metals, without exception, can be boiled under atmospheric pressure in the electric furnace, the temperature of which is probably not greater than 3500° C.

Carnelley has published a series of important papers,[3] dealing with the melting points of the elements, and has shown that, like the specific gravities, these also are periodic functions of the atomic weight. This is readily seen from the following

[1] *Ber.*, 1905, **38**, 262.

[2] *Compt. rend.*, 1906, **142**, 189, 425, 673.

[3] Published in *Journ. Chem. Soc.*, *Proc. Roy. Soc.*, and *Phil. Mag.* from 1876 onwards.

table (p. 65) taken from one of Carnelley's papers,[1] with some modifications of the numbers, rendered necessary by more recent determinations of the melting points of some elements. The numbers are in many cases only approximate, and all are given in absolute temperatures, taking $-273°$ C. as zero.

If the melting points are mapped out in the same manner as the atomic volumes, a periodic curve is obtained, in which, however, the maxima occur in the centre of the second and third periods, and afterwards in the centre of the double periods, whilst the minima occur at the ends.

Carnelley has further shown that the melting points of analogous compounds of the elements exhibit the same periodic variation with the atomic weight as those of the elements themselves.

(3) Conductivity of Metals.

34 The conductive power of the metals for heat and electricity, which is almost invariably far greater than that of the non-metals and all chemical compounds, varies considerably also in the different metals, and even in the same metal, according to its physical condition and chemical purity. The order of conductive power of the metals is the same for both heat and electricity, a fact first pointed out by Forbes[2] in 1833. Generally speaking, the soft metals conduct best, and the conductivity of all metals becomes lower as the temperature rises. Dewar and Fleming[3] have shown that, as the temperature is lowered, the conductivity of all metals tends to become more nearly equal, and the curves representing the conductivity at different temperatures indicate that at the absolute zero the conductivity of all of them would become perfect, or, in other words, at that temperature the resistance would be *nil*.

These properties, as well as almost all the other physical properties of the element, such as volatility, magnetic and diamagnetic properties, heats of formation of compounds, thermal expansion, formation of coloured ions, and even elasticity and breaking strain, indicate the same general periodic variation as has already been shown for the specific gravity, compressibility, and melting point; space will not permit the discussion of these here, but for details reference

[1] *Phil. Mag.*, 1879 [5], **8**, 315. [2] *Phil. Mag.*, 1833, **4**, 27.
[3] *Phil. Mag.*, 1893 [5], **36**, 271.

0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
	H 14°									
He <H	Li 452°	Gl <1230°	B v. h.	C v. h.	N 62·5°	O 46°	F 40°			
Ne <A	Na 371°	Mg 923°	Al 930°	Si c. 1690°	P yel. 317° red c. 620°	S 386°	Cl 171°			
A 85°	K 335°	Ca 1073°	Sc ?	Ti v. h.	V c. 1953°	Cr c. 1820°	Mn c. 1513°	Fe c. 1793°	Co 1763°	Ni 1725°
	Cu 1356°	Zn 692°	Ga 303°	Ge c. 1231°	As ?	Se 490°	Br 266°			
Kr 104°	Rb 311°	Sr c. 1073°	Yt ?	Zr >Si	Cb c. 2223°	Mo c. 2380°	—	Ru >2200°	Rh >2000°	Pd 1822°
	Ag 1234°	Cd 594°	In 428°	Sn 505°	Sb 903°	Te 728°	I 386°			
Xe 133°	Cs 300°	Ba 1123°	La 1083°	—	—	—	—	—	—	—
	—	—	—	—	—	—	—			
—	—	—	—	—	Ta c. 2523°	W >Mo	—	Os v. h.	Ir c. 2570°	Pt 2023°
	Au 1337°	Hg 234°	Tl 576°	Pb 600°	Bi 543°	—	—			
Nt	—	Ra	—	Th ?	—	U >Fe	—	—	—	—

v. h. = very high. c. = about.

may be made to Lothar Meyer's "Modern Theories of Chemistry," translated by Bedson and Williams (Longmans).[1]

35 There is, however, one important physical property which does not exhibit this periodic variation, viz., the atomic heat. As already shown (p. 16), this is approximately constant, and the fact is made use of in determining the true atomic weight of an element from its equivalent. The exceptions to this rule are found among those elements of low atomic weight which fall below an oblique line drawn across Lothar Meyer's diagram from the commencement to the vertical line representing an atomic weight of 40 (see table, p. 60), whilst those above the line follow the law. Without reference to the diagram, this may be expressed by saying that of the elements having an atomic weight of less than 40, only those agree with Dulong and Petit's rule at the ordinary temperature, whose sp. gr. in the solid state is less than 1·75.

Correction of Doubtful Atomic Weights.

36 The periodic arrangement of the elements has proved of great value in checking doubtful atomic weights. In 1869, when Mendeléeff first promulgated his theory, the atomic weights then accepted for many elements did not allow of their being placed in a position corresponding to their properties, and Mendeléeff boldly concluded that in such cases either the equivalent had been wrongly determined, or an incorrect multiple of the latter had been taken for the atomic weight. In almost every instance subsequent research has justified this conclusion. Thus, for example, the atomic weight of molybdenum was given by some chemists as 92, and by others as 96, and, as the former figure placed the metal before the pentavalent columbium, Mendeléeff adopted the number 96, which placed it in the same group as chromium; this is now the accepted value. Again, the atomic weights of the four elements, gold, platinum, iridium, and osmium, were at that time taken as Au 195·2, Pt 195·7, Ir 195·7, and Os 197·6, whereas according to the requirements of the periodic system

[1] See also Rudorf, *The Periodic Classification and the Problem of Chemical Evolution* (London and New York, Whittaker & Co., 1900); Richards, Faraday Lecture, *Journ. Chem. Soc.*, 1911, **99**, 1201.

the order should be reversed, osmium having the lowest and gold the highest atomic weight; this also has been proved by the redeterminations made by Lothar Meyer and Seubert, Thorpe and Laurie, and Krüss, the numbers now adopted being Os 190·9, Ir 193·1, Pt 195·2, and Au 197·2.

The atomic weight of indium was at first taken as 75·2, and the formula of the chloride as $InCl_2$, but for an element of this atomic weight no place was available in the periodic system; if, however, the formula of the chloride is taken as $InCl_3$, the atomic weight becomes 112·8, and the element then falls naturally between cadmium and tin, and in the same group as aluminium. Determinations of the specific heat of the metal and the vapour density of the chloride have subsequently proved the correctness of the supposition. Uranium was formerly supposed to have an atomic weight of 60, and later, of 120, neither of these numbers fitting into the periodic system. The metal, however, falls in naturally if the atomic weight be about 240, and this was confirmed by Roscoe's determination of the vapour density of uranium chloride, UCl_5, and by Zimmermann's determination of the specific heat of the metal. Another element whose atomic weight was doubtful was glucinum, which was regarded by some as a divalent metal of atomic weight 9, and by others as a trivalent metal of atomic weight 13·5. The determination of the vapour density of glucinum chloride has now shown that this has the formula $GlCl_2$; the atomic weight must therefore be 9, which agrees with the demands of the periodic system.

37 In the table given above (pp. 50–51) the sequence of atomic weights has been broken in three places in order to maintain certain elements in the groups to which their chemical and physical properties assign them; argon (39·88) precedes potassium (39·10); tellurium (127·5) precedes iodine (126·92); and cobalt (58·97) precedes nickel (58·68). The chemical properties of argon and tellurium are so well marked that there seems no doubt that these elements have been correctly placed, and there is at least a possibility that more extended investigation may show that their atomic weights are not so high as they are at present thought to be. Cobalt is usually placed before nickel, both on account of its physical and chemical relations to iron and nickel, and because of the close analogy which many of its compounds present to those of rhodium and iridium. These reasons cannot, however, be considered as

having the same weight as those which apply to argon and tellurium.[1]

Existence of Unknown Elements.

38 The arrangement of the elements according to the periodic system leaves, as already seen, a number of blanks, which Mendeléeff assumed were to be filled by elements then undiscovered, and he suggested that, from the properties of the elements with the next highest and lowest atomic weights, and from those of the other members of the same group, it was possible to predict very closely the properties such elements would have when discovered. Thus, for instance, were selenium unknown, its properties could be largely predicted from those of arsenic and bromine on the one hand, and of sulphur and tellurium on the other, these elements being termed by Mendeléeff the "atom analogons" of the element in question. At that time there were three gaps for elements with atomic weights less than 75, namely, one having an atomic weight of 44, corresponding to boron, one of atomic weight about 69, corresponding to aluminium, and one of atomic weight 72, corresponding to silicon. To these hypothetical elements Mendeléeff gave the names Ekaboron, Ekaluminium, and Ekasilicon (from the Sanskrit *Eka*, one), and, proceeding in the manner indicated, he gave in considerable detail the properties such elements would possess. In less than twenty years his predictions were completely verified by the discovery of gallium by Lecoq de Boisbaudran in 1875, of scandium by Nilson in 1879, and of germanium by Winkler in 1887. The first is Mendeléeff's ekaluminium, the second ekaboron, and the third ekasilicon, and the striking manner in which the forecast was fulfilled in each case may be seen from the following table, in which the predicted properties and those actually observed are arranged in parallel columns.

Ekaboron.	Scandium.
At. wt. 44.	At. wt. 44·1.
Oxide Eb_2O_3, sp. gr. 3·5.	Sc_2O_3, sp. gr. 3·86.
Sulphate $Eb_2(SO_4)_3$.	$Sc_2(SO_4)_3$.
Double sulphate not isomorphous with alum.	$Sc_2(SO_4)_3.3K_2SO_4$—slender prisms.

[1] For a discussion of the evidence bearing on the atomic weight of tellurium, see Vol. I., p. 483.

Ekaluminium.	Gallium.
At. wt. 68, sp. gr. 6·0.	At. wt. 69·9, sp. gr. 5·92.
Ekasilicon.	Germanium.
At. wt. 72, sp. gr. 5·5.	At. wt. 72·5, sp. gr. 5·46.
Oxide, EsO_2, sp. gr. 4·7.	Oxide, GeO_2, sp. gr. 4·7.
Chloride, $EsCl_4$, liquid, boiling slightly below 100°, sp. gr. 1·9.	Chloride, $GeCl_4$, liquid, boiling at 86°, sp. gr. 1·887.
Ethide, $Es(C_2H_5)_4$, liquid, boiling at 160°, sp. gr. 0·96.	Ethide, $Ge(C_2H_5)_4$, liquid, boiling at 160°, sp. gr. slightly less than that of water.
Fluoride, EsF_4, not gaseous.	Fluoride, $GeF_4{\cdot}3H_2O$, white solid mass.

39 From the above it will be seen that the periodic system of classification rests on a very firm basis, the successful prediction of the properties of undiscovered elements forming very strong evidence in favour of the general plan. In certain respects the system will doubtless undergo modification as our knowledge increases, for difficulties occur which cannot at present be explained. Thus there are elements sometimes in the same group between which only a limited amount of analogy can be traced, and, on the other hand, elements which have a good deal in common are sometimes separated widely. The members of the higher periods often show considerable deviation in properties from the corresponding members of the lower periods, but when the very numerous gaps existing in the former shall have been filled up, and the elements at present only slightly known are more accurately investigated, these relations will perhaps become more plain.

Only four of the numerous metals of the rare earths (Sc, Yt, La, and Ce) are assigned definite places in the foregoing tables, and the problem as to the relation of the remaining members of this family to the periodic classification has given rise to much discussion. In the prevailing uncertainty as to the individuality of many of the substances of this class hitherto described, and in the absence of any complete knowledge of the physical and chemical properties of the metals themselves, it is impossible at present to express any decided opinion. It has, however, been suggested[1] that in this family of elements certain positions in the periodic system are occupied not by a single element, but by

[1] See Brauner, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 142; Biltz, *Ber.*, 1902, **35**, 562,

a group of elements differing very slightly in atomic weight and chemical properties.

A further difficulty is found in the anomalous position of hydrogen, which forms the sole member of the first series at present known, and which in its properties differs to so great an extent from all other known elements. It resembles the alkali metals inasmuch as it is monovalent and strongly electropositive, but differs very greatly from them in other respects. On the other hand, it has been maintained[1] that hydrogen as a monovalent, diatomic gas falls naturally at the head of the halogen group, and the great similarity in properties of the hydrocarbons to their halogen substitution derivatives is adduced as evidence of chemical analogy between hydrogen and the halogens. This relation, moreover, appears to accord better with the sequence of atomic weights, the difference between hydrogen and fluorine being 18, whilst that between hydrogen and lithium is 6, a much lower number than is observed elsewhere between two members of a vertical group.

Mendeléeff himself regards hydrogen as standing at the head of group I., and as being one of a series consisting of two elements only, the missing element being a member of the helium family, of atomic weight less than 0·4. Mendeléeff further suggests[2] that this element may be identical with the unknown element coronium, to which certain lines of the spectrum of the outermost region of the solar corona have been ascribed. He has also put forward the surmise that the ether itself may in reality be composed of atoms of an element of about one-millionth of the atomic weight of hydrogen, which he places in a zero series preceding that containing hydrogen.

Many attempts have been made to modify Mendeléeff's table, so as to reduce the number of anomalies and bring out more clearly the relations between the elements, but none of these proposals has as yet been generally accepted.[3]

[1] Orme Masson, *Chem. News*, 1896, **72**, 283.

[2] *Principles of Chemistry*, Vol. II. Appendix III. (Longmans, Green, and Co., London, 1905).

[3] See on this point, Rudorf, *The Periodic Classification and the Problem of Chemical Evolution* (Whittaker and Co., London and New York, 1900), where references to the literature up to 1900 will be found; Werner, *Ber.*, 1905, **38**, 914; Armstrong, *Proc. Roy. Soc.*, 1902, **70**, 86; Reynolds, *Journ. Chem. Soc.*, 1902, **81**, 612; Zengelis, *Chem. Zeit.*, 1906, **25**, 294; Schmidt, *Zeit. physikal. Chem.*, 1911, **75**, 651; Baur, *ibid.*, 1911, **76**, 569; Sanford, *J. Amer. Chem. Soc.*, 1911, **33**, 1349.

CRYSTALLINE FORM OF METALS.

40 Most metals, as well as their alloys, can be obtained in the crystalline state, and those occurring as minerals in the native condition are often found crystallised; this is the case with gold, silver, copper, platinum, iridium, palladium, gold-amalgam, and silver-amalgam. In general, the form which they assume is one belonging to the regular system, such as the octahedron or the cube, or a combination of these forms. Some few, such as zinc, antimony, and bismuth, crystallise in the hexagonal system, and the two latter metals, which closely resemble arsenic, are found, as this is, crystallised in rhombohedra. On the other hand, a few metals, such as tin and potassium, crystallise in the tetragonal system.

To obtain metals in the crystalline state several processes can be adopted. Crystals of metals which fuse readily can be obtained by solidification after fusion. Bismuth, antimony, lead, and tin may thus be crystallised, and, in a similar way, sodium and potassium; in the latter cases air must of course be excluded. Metals which are easily volatilised, such as zinc, cadmium, and potassium, may be obtained in crystals by condensation from the gaseous state, whilst other metals, such as silver, thallium, and lead, can be readily crystallised by the electrolysis of solutions of their compounds. The metals separate out in lustrous crystalline plates, and the exhibition of this phenomenon on the screen forms one of the most striking and beautiful of lecture-room experiments. The crystallisation of metals is well illustrated also by the formation of the lead-tree when a piece of zinc is immersed in a solution of lead acetate.

The fracture of metals is an important characteristic intimately connected with the crystalline form, and in many instances it is of importance as giving a knowledge of the purity, or otherwise, of the metal. The following varieties of fracture are generally recognised:—

(1) Crystalline fracture; as in antimony, bismuth, zinc, spiegel-iron, &c.

(2) Granular fracture; as in grey forge pig-iron.

(3) Fibrous fracture; as in bar and wrought iron when partly broken by bending.

(4) Silky fracture; as in a piece of tough copper.

(5) Columnar fracture; as observed in the grain tin of commerce.

(6) Conchoidal fracture; noticed in the cases of native arsenic and certain brittle alloys, such as that composed of one part of copper to two of zinc (Percy).

COLLOIDAL SOLUTIONS OF METALS

41 When dilute solutions of many metallic salts are treated with reducing agents, the metal which is produced is not precipitated in the solid form, but remains dissolved in the colloidal state (Vol. I., p. 916). In this way Faraday, as early as 1857, by reducing solutions of gold chloride with phosphorus, succeeded in preparing red-coloured solutions of gold, which could be preserved for many years without depositing any of the metal. Such solutions can be freed from the other products of the reduction and from the excess of reducing agent by dialysis, and then form coloured liquids, which are often stable for a long period, and exhibit in a very characteristic manner the properties of colloidal solutions. They can be boiled as a rule without any metal separating out, and can in some cases, such as that of gold reduced by quinol, be evaporated to dryness, leaving a residue which is soluble in water and retains its solubility even when preserved for a considerable time in the dry state. The metal is precipitated in the insoluble form (coagulated) when soluble electrolytes are added to the solution, and is deposited in the solid state at the anode when a current of electricity is passed through the liquid, whereas in the electrolysis of a metallic salt the metal is deposited at the cathode. As already mentioned, the metal will not diffuse through a colloid membrane, and in many respects these solutions present an extremely close analogy with the solutions of the organic colloids, substances which usually possess a very high molecular weight.

Investigation with the ultramicroscope shows that the colloidal solution of a metal consists of extremely minute particles of the metal in a state of suspension. These are in constant motion, the rate of movement increasing as the size of the particles diminishes.[1]

The reducing agents which have been found most suitable for the production of colloidal metals are phosphorus, hypophos-

[1] See Zsigmondy's *Colloids and the Ultramicroscope.*

phorous acid, ferrous sulphate, hydroxylamine hydrochloride, hydrazine hydrate, formaldehyde, quinol, pyrogallol, and other similar substances.[1]

Another extremely interesting method of preparing colloidal solutions of the metals consists in setting up an electric arc between two poles of the metal under water or very dilute alkali.[2] In these circumstances pulverisation of the cathode occurs, and the finely divided metal thus produced remains in colloidal solution in the water. In this way, for example, almost opaque dark-coloured solutions, containing a maximum of 0·015% of platinum, and bluish-violet solutions of gold of similar concentration, as well as solutions of silver, iridium, and cadmium, can readily be prepared. A number of other metals, including mercury, copper, iron, nickel, and zinc, can be brought into colloidal solution by a slight modification of this method, which consists in employing a thin layer of the metal, deposited on the surface of another metal, as the cathode.

The solutions of platinum obtained in this way promote the combination of hydrogen and oxygen at ordinary temperatures, and decompose hydrogen peroxide in the same way as does platinum black. In its behaviour towards hydrogen peroxide colloidal platinum is strikingly similar to certain organic enzymes, and has accordingly been described by Bredig as "an inorganic ferment."

The stability of solutions of these metallic colloids is much increased by the presence of other colloids such as gelatin. Advantage has been taken of this property, in some cases, by preparing the colloidal metal in the presence of, or even by the reducing action of, an organic colloid. Thus, Carey Lea has described a number of colloidal forms of silver produced in the presence of dextrin and similar substances, whilst Paal has prepared several metals in a remarkably stable colloidal form in presence of certain products of the decomposition of egg albumin by alkalis. The colloidal forms of certain refractory metals, such as osmium and tungsten, have been employed in the manufacture of filaments for electric lamps.

The specific properties of the different colloidal metals will be found under the heading of the metals concerned.

[1] For details see Svedberg's *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe* (Theodor Steinkopff; Dresden, 1909); Wo. Ostwald's *Grundriss der Kolloidchemie* (Steinkopff).

[2] Bredig, *Zeit. Electrochem.*, 1898, **4**, 514; *Zeit. angew. Chem.*, 1898, 954; *Anorganische Fermente* (Engelmann, Leipzig, 1901).

ALLOYS AND AMALGAMS.

42 Especially characteristic of the metals as a class are the mixtures and compounds which different metals form with one another, and to which the name of alloy is given (derived through the French from the Latin *alligare*, to bind to). Amongst chemical compounds in general, those are found to be most stable, and to show the greatest amount of chemical individuality, whose constituents are the most diverse. In the case of the alloys, however, the essential properties of the metals are uniformly reproduced. Thus, they all possess metallic lustre and they conduct heat and electricity well, even when they assume distinct crystalline forms and contain their constituents in the proportion of their combining weights. Hence alloys are distinguished from the compounds which the metals form with such elements as oxygen, sulphur, and chlorine, in which the general properties of the metals have undergone a complete change. So great indeed is the resemblance between the alloys and the metals proper that in all ages, in common parlance, they have been confused under the same name. The early Greek alchemists classed electrum, an alloy of gold and silver, amongst the metals, giving to it the sign of Jupiter, and even nowadays the word metal is often employed to designate an alloy.

The union of metals to form alloys may be brought about in several different ways, of which only four will be mentioned.

(1) By fusing together the constituent metals.
(2) By strong compression of the finely powdered metals.
(3) By electro-deposition.
(4) By the simultaneous reduction of the constituent metals.

The first method is by far the most important of the four, as almost all alloys are produced in this way on the large scale. The second method has not received any, and the third only a limited technical application, whilst the fourth is the primitive method by which brass and other alloys were first produced, and which has certain applications at the present time. These may therefore be shortly discussed before passing on to the consideration of the first and chief method.

Compression.—The union of powdered metals to form alloys when strongly compressed was first observed by Spring,[1] who

[1] *Bull. Acad. roy. Belg.*, 1878, **45**, No. 6; 1880, **49**, No. 5; *Ber.*, 1882, **15**, 395.

subjected the mixed powders to pressures up to forty tons per square inch in a steel cylinder, and in this manner obtained alloys identical with those obtained by fusion. It might be supposed that the union is effected by the heat evolved during the compression causing the metals to melt; but Spring has shown that this is not the case, since, if the whole of the work done in the compression were converted into heat, this would still be insufficient to effect the fusion of the mass.

Electro-deposition.—Just as copper can be deposited from solutions of its salts by electrolysis, so it is sometimes possible to deposit two metals simultaneously from a mixture of their salts, so that they unite to form an alloy. Thus, by electrolysing under suitable conditions a solution containing certain zinc and copper salts, brass is obtained.

Simultaneous reduction of metals.—By this method brass was made long before the metal zinc was known in the free state, and, more recently, "calamine brass" has been made by the reduction of calamine in the presence of copper. At the present time this method is used in the production of alloys by the treatment of metallic waste and slags; in the manufacture of ferro-manganese and spiegeleisen in the blast furnace; in that of ferro-chrome, ferro-aluminium, etc., in the electric furnace; and in the manufacture of certain alloys by the Goldschmidt or "thermit" process.

Preparation of Alloys by Fusion.—The method of making alloys by fusion varies according to the nature of the metals to be alloyed. If none of the constituent metals is very volatile, they may be mixed and fused together, but if one of the constituents be a volatile metal, such as zinc, the other constituent or constituents are melted, raised to a sufficiently high temperature to cause the zinc to melt and mix easily, the zinc is then added and the whole stirred. The metals are generally covered with a layer of carbon to prevent oxidation during the process.

When metals are melted together they do not always form a homogeneous product, and a metallic alloy is defined as a mixture of metals which, after melting, does not separate into two layers. When such a separation does occur, each layer becomes a distinct alloy. For example, when lead and zinc are melted together and allowed to cool slowly, they separate into two distinct layers, the bottom one being an alloy of lead and zinc, containing 1·3 per cent. of zinc, and the top

one an alloy of zinc and lead containing 1·57 per cent. of lead.

43 The following seems to be the most convenient method of classifying alloys:—

a. Perfect alloys, which are absolutely homogeneous when in the solid state, *e.g.*, the gold-silver alloys.

b. Intermediate alloys, which are not absolutely homogeneous, but are composed of the separate constituents in a microscopic state of division in juxtaposition, *e.g.*, the alloy of lead and tin of lowest melting point.

c. Imperfect alloys, which are by no means homogeneous, one or more of the constituents having crystallised out in advance of the others, producing a more or less imperfect but regular admixture in the cold metal, *e.g.*, the lead-antimony alloy containing 10% of antimony.

Alloys containing only two metals are known as binary, those containing three as ternary, &c.

THE STUDY AND EXAMINATION OF ALLOYS.

44 The most important modern methods of research on this subject may be summarised as follows:—

1. Chemical methods. Analysis and separation of the constituents.

2. Thermal methods. Determinations of melting points, and critical changes.

3. Microscopical methods. Examination of crystalline and internal structure.

4. Mechanical methods. Determination of elasticity, tenacity, ductility, &c.

5. Electrical methods. Determination of resistance and E.M.F.

6. Magnetic methods. Examination of the various changes in magnetic properties during heating and cooling.

Illustrations will be given of only two of these methods, viz., the Thermal and the Microscopical.

Examination of Alloys by the Thermal Method.—The melting point of an alloy is usually lower than those of the metals which compose it. This is well seen in the case of ordinary plumbers' solder, consisting of tin and lead, which melts more easily than either of the constituent metals. This fact was known so

long ago as the time of Pliny, for he states that tin cannot be soldered without lead, nor lead without tin, and that lead tubes are soldered with a mixture of one part of tin and two parts of lead, a mixture which is used at the present day. Homberg, in 1669, recommmended an alloy of equal parts of tin, lead, and bismuth for sealing up anatomical preparations; and in 1772[1] Valentine Rose the elder discovered the well-known fusible metal which bears his name. This consists of one part of tin, one part of lead, and two parts of bismuth. It melts at 94°, the lowest melting point among the constituents being that of tin, viz., 232°. Another alloy, consisting of eight parts of lead, fifteen of bismuth, four of tin, and three of cadmium, softens at a temperature of 60° and is perfectly liquid at 65°, the melting points of its constituents being tin 232°, bismuth 270°, cadmium 321°, and lead 327°.[2]

45 For the experimental investigation of the relation between the freezing point and the composition of the alloy formed by two or more metals, a pyrometer, such as the thermo-couple pyrometer or the electric-resistance pyrometer, is required. The rate of cooling of a quantity of the alloy is then determined and plotted in a curve, any breaks in which indicate points of solidification or other critical changes. A complete series of alloys, such as those of lead and tin, is generally studied together and the points so obtained on the "cooling-curves" are employed for the construction of a second curve which shows the variation in the freezing point with change of composition and forms the freezing point curve of the series.

Thermal Classification of Binary Alloys.[3]—From the general form of the freezing point curves, binary alloys may be divided into groups as follows:—

Group 1. The curve consists of two branches, starting from the melting points of the pure metals and meeting at a point corresponding to the eutectic alloy. A eutectic alloy is that alloy of any series, or range of series, which has the lowest melting point, and corresponds to the cryohydrate formed by cooling a solution of a salt in water (Vol. I., p. 310). In some series of alloys more than one eutectic is found, but in such a case, each of them corresponds to a different set of constituents.

[1] *Stralsund Magazine*, 1772, 2.

[2] Lipowitz, *Dingl. Poly. Journ.*, 1860, **158**, 376.

[3] *Alloys*, H. le Chatelier, *Metallographist*, Vol. I., 1898, p. 94. See also *Metallography*, by C. H. Desch (Longmans & Co., 1910).

The melting point of a eutectic mixture is lower than that of either constituent.

This type of curve obtains when the metals form neither definite compounds nor isomorphous mixtures, and is illustrated in Fig. 3. This represents the freezing point curve of the lead-tin series, the lines AX and BX corresponding to the separation of lead and tin respectively, and X being the point of solidification of the eutectic alloy. The horizontal line CXD represents the range of the series in which eutectic mixtures will be found, it having been observed that very dilute solutions of tin in lead solidify completely before the eutectic temperature is reached.

As long as the amount of lead present is above 31 per cent., metallic lead separates out first when the liquid alloy is cooled;

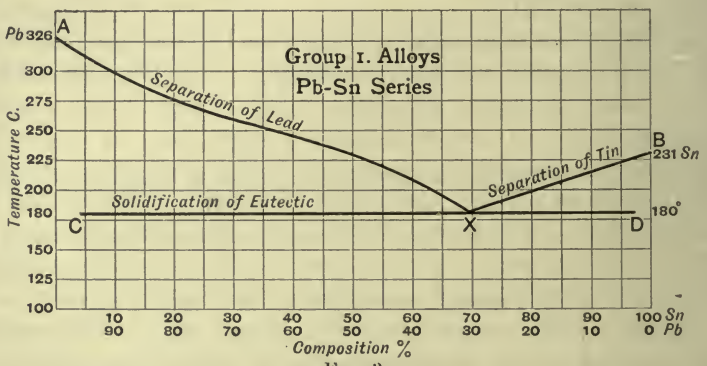


FIG. 3.

if the amount of lead is below this, metallic tin separates out. The alloy containing 31 per cent. lead and 69 per cent. tin is the eutectic alloy, and solidifies at 180°, in which point the curves representing the separation of lead and tin intersect.[1]

The most important members of this group are the alloys of:—

Pb and Sn; Zn and Sn; Pb and Sb; Bi and Sn;
Pb and Ag; Zn and Cd; Cu and Ag; Cu and Bi.

Group 2. The curve consists of three branches, two of them starting from the melting points of the pure metals, the third exhibiting a maximum, and intersecting the others in two points corresponding to two eutectics. This obtains when the two metals form a definite compound; in such cases the curve

[1] See also Rosenhain and Tucker, *Phil. Trans.*, A, 1908, **209**, 89.

may be divided into two portions, each comparable to Group 1. In Fig. 4, which illustrates this type of curve for the series Cu and Sb, AX represents the separation of copper, XB the separation of the compound $SbCu_3$, and EXF the range of the corresponding eutectic, which consists of a mixture of Cu and $SbCu_3$. The point B represents the melting point of the alloy containing 38·5 per cent. of antimony, which is a white

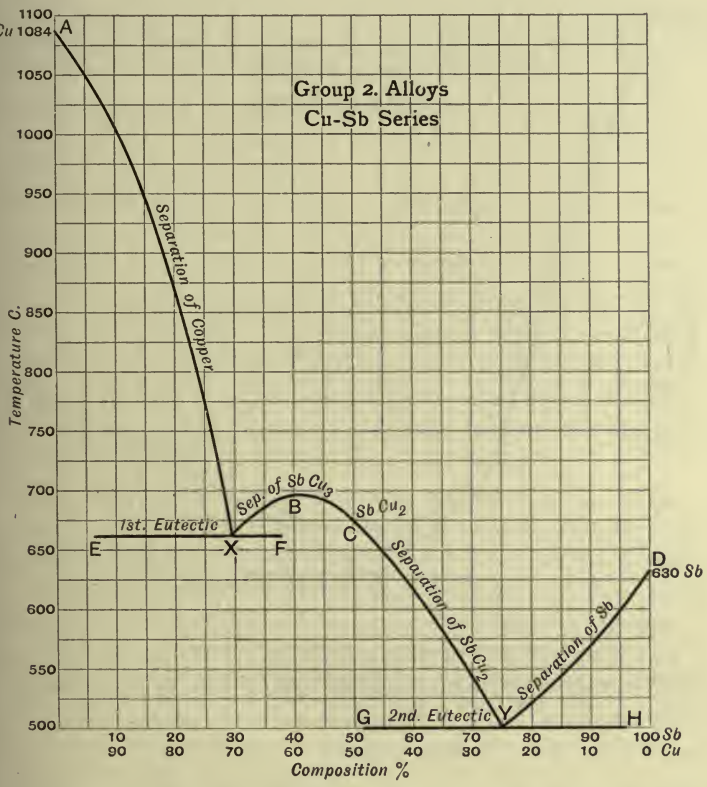


Fig. 4.

compound having the formula $SbCu_3$. Beyond this point the curve departs from the simple type, and between B and C a mixture of $SbCu_3$ and $SbCu_2$ separates out, C representing the melting point of this second compound, which is purple in colour. The lines CY and DY correspond to the separation of the compound $SbCu_2$ and metallic antimony respectively, Y being the melting-point of the second eutectic, which consists of a mixture of antimony and $SbCu_2$, and has a range repre-

sented by the horizontal line GYH. To this group belong also the alloys of Mg and Pb; Ni and Sn.

Group 3. The curve of fusibility is continuous and unites the melting points of the two metals. This occurs when the metals form isomorphous mixtures. To this group belong the alloys of Bi and Sb; Ag and Au; Ni and Co; Cu and Ni; Au and Cu.

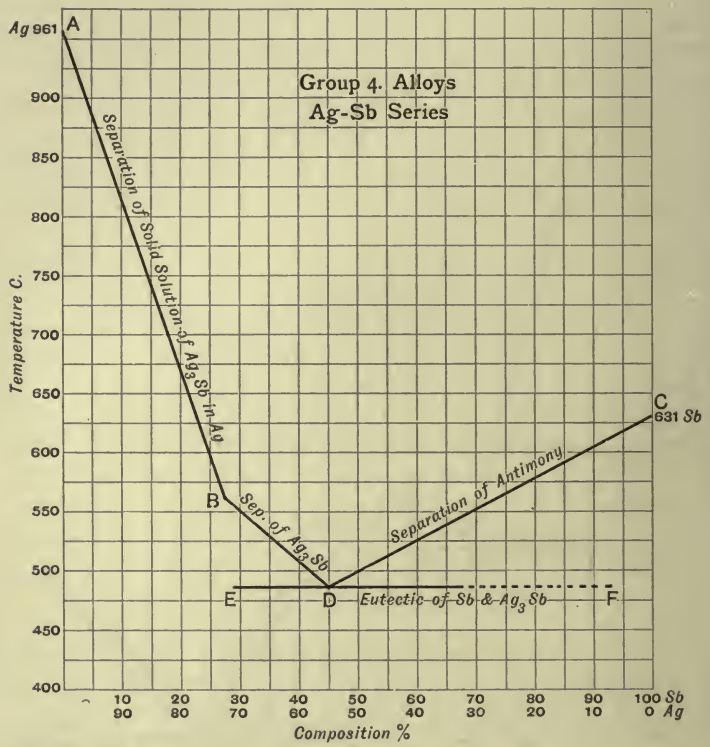


Fig. 5.

Group 4. The curve consists of two branches, starting from the melting points of the metals as in Group 1, but on one branch there is a point at which a change of direction occurs, indicating the formation of a definite compound.

Fig. 5 illustrates this type of curve for the silver-antimony series. The line AB corresponds to the separation of solid solutions of the compound Ag_3Sb in Ag, and the point B represents the formation of this compound; the lines BD and CD represent the separation of Ag_3Sb and antimony respectively. D is the eutectic point, and the line EDF indicates

the range of the eutectic, which consists in this case of a mixture of Ag_3Sb and antimony. To this group belong also the alloys Sn and Ag; Al and Ag; Sb and Sn.

Group 5. Alloys with abnormal curves of fusibility, such as those of Cu and Sn, Cu and Zn, Sb and Sn, Zn and Ag, Al and Au.

46 *The Examination of Alloys by the Microscope.*[1]—By examining a suitably prepared specimen by reflected light evidence may be obtained on the following points:—

Crystalline state of the metal or alloy.

Constitution of the alloy.

Presence of foreign bodies.

Presence of flaws, blow-holes, or cracks.

Presence of eutectics.

Preparation of Specimens.—In order to carry out this examination successfully, much care is necessary in the preparation of the specimen. A small piece is cut by means of a hack-saw, and smoothed with files; after this the specimen is rough-polished on emery cloth, and then finished on a series of graded emery papers, such as the French papers marked 0, 00, 000, and 0000.

When the specimen is free from scratches, the surface is treated by some agent which will attack the separate constituents differently as a preliminary to microscopic examination. For this purpose simple attack by some reagent, such as nitric, sulphuric, or hydrochloric acid, iodine, potassium cyanide, or ammonia may be used. By this means one constituent may be dissolved more quickly than another, or may be coloured differently, or the joints between adjacent crystals may simply be eaten away. Heat-tinting is another method used, and consists in gently heating the polished surface, whereby the more oxidisable constituents become coloured by oxide tints.

The evidence obtained in this way as to the structure of the alloy is of great value, and is illustrated by the following typical examples:—

Fig. 6 represents the appearance (under a magnification of 100 diameters) of a case-hardened piece of steel which has been quenched, and the specimen polished and then etched with picric acid. The wide black mark running across is a crack which developed during quenching; above this is seen

[1] See also *Alloys*, by E. F. Law (C. Griffin & Co.).

the structure of saturated steel, containing 0·9 per cent. of carbon. This is known as martensite, and if slowly cooled from a red heat would have formed the eutectoid pearlite (p. 84). Below the crack is seen the structure of super-saturated steel; the black lines consist of carbide of iron, Fe_3C, contained in the ground-mass of martensite.

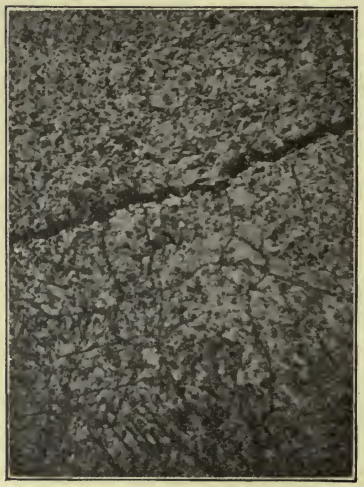


Fig. 6.

Fig. 7.

Fig. 7 is a photomicrograph (magnification 100 diameters) of a Sn-Sb-Cu alloy, containing Sn 83 per cent., Sb 11 per cent., Cu 6 per cent. The large white cubes are crystals of the compound SnSb, the smaller crystals consist of $SbCu_3$, and the dark ground-mass consists of tin containing a small quantity of antimony in solution.

The Constitution of Metallic Alloys.

47 As a result of the numerous researches carried out by the methods indicated above, it is concluded that the possible *constituents* of solid metallic alloys are very varied, the most important being the following[1]:—

1. Free metals in the pure state.
2. A solid solution of one metal in another.
3. A solid solution of a definite chemical compound in an excess of metal.

[1] "Metallic Alloys," J.E. Stead, Cleveland Institution of Engineers, 1900 (*Metallographist*, 1902, **5**, 110).

4. Eutectic mixtures.

5. Definite chemical compounds of metals with metals.

6. Definite chemical compounds of metals with certain non-metals.

7. Allotropic modifications of metals.

1. *Free metals in the pure state.*—These are metals which separate from solution, or crystallise in the pure state. They are found in alloys as *crystallites* (*i.e.*, indefinitely crystalline, or incipient forms of crystallisation of the metals), or as perfectly formed crystals, which are produced only when the metal in question is incapable of holding in solid solution one of the other constituents of the alloy. An example of this is afforded by the Pb-Ag alloys containing about 1 per cent. of silver.

2. *Solid solution of one metal in another.*—A solid solution is defined as a homogeneous mixture of two or more substances in the solid state, and solid solutions of one metal in another, when crystalline, are solid isomorphous mixtures or mixed crystals.

Many metals which mix with each other in the liquid state do not remain in solution when solidification occurs; the solids thus formed are called solidified or congealed solutions. It is very important to distinguish between these and the true solid solutions.

Solid solutions crystallise in a form identical with, or very closely approximating to, that of the constituent which predominates. Examples of this are found in the Au-Ag and Ni-Co series.

3. *Solid solution of a definite chemical compound in an excess of metal.*—In many alloys definite chemical compounds are formed, and in some cases these compounds are dissolved in the metal which is in excess, forming a solid solution. Examples of this are found in the Cu-Sn, and Au-Al series.

In the same manner, some non-metallic elements combine with a portion of one of the metals, forming a compound which is dissolved, under suitable conditions, in the excess of metal. Examples are afforded by the behaviour of carbon and phosphorus in iron.

4. *Eutectic mixtures.*—The composition of eutectic mixtures is constant, and, within certain limits, independent of the original proportions of the constituent metals; the composition is not generally in simple atomic proportions, although it sometimes approximates very closely to these. This is the case

with the well-known Levol's alloy of the composition Cu 28·1 to Ag 71·9, a relation which practically corresponds with the formula Cu_2Ag_3: and this accounts for the fact that this alloy has been mistaken for a definite chemical compound.

A eutectic consists of a conglomerate of distinct particles of the components, mechanically mixed. These components may be two or more metals which do not chemically unite, one metal and a definite chemical compound, two or more chemical compounds, one free metal and a solid solution, one compound and a solid solution, or two solid solutions.

The pearlite formed in solid steel, when it cools slowly from above 700° C. to 600° C., is a solid solution of carbon in iron above 700°, but splits up into two constituents on cooling, and is known as a *eutectoid*, to distinguish it from an ordinary eutectic.

5. *Definite chemical compounds of metals with metals.*—Many metals unite chemically in atomic proportions forming compounds which are quite homogeneous, and are recognised by having certain characteristics different from those of the component metals, the colour, hardness, crystalline form, &c., being often quite distinct. Sometimes, on bringing the metals together in the molten form, great heat is evolved, an almost certain sign of chemical action. Thus aluminium and copper combine to form a golden yellow compound, Cu_3Al, harder, stronger, and tougher than either metal, and also than the compounds $CuAl_2$ and CuAl.

6. *Definite chemical compounds of metals with non-metals.*—In many cases metals combine with non-metals to form definite chemical compounds, which are of considerable importance in commercial alloys. Undoubtedly the most important of these compounds is the carbide of iron, Fe_3C, the amount and condition of which determine most of the valuable properties of steel.

Iron combines also with phosphorus to form phosphides; zinc with arsenic and phosphorus to form white compounds; and copper with phosphorus to form a pale yellow compound.

7. *Allotropic modifications of metals.*—The addition of very small quantities of another element frequently brings about a great change in the properties of a metal, although the quantity of the former added is too small to allow of the supposition that a true compound is formed. Thus, for example, the conductivity of copper is very greatly affected

by the presence of extremely small percentages of foreign metals such as tin, and the hardness and tenacity of metals are also greatly altered by small quantities of other elements. Matthiessen was, therefore, led to the conclusion that when a metal is alloyed with small quantities of another, the former frequently undergoes a molecular change, and is converted into an allotropic modification showing very different properties.

It is by no means easy to determine whether an allotropic change has taken place, and there is still much to be learned about the effect of dissolving one metal in another, and about the grouping of atoms in solid solutions.

The following facts appear to point to the probability of metals occurring as allotropic modifications in alloys.

(*a*) If a small piece of potassium-gold alloy, containing 10 per cent. of gold, is thrown upon water, the potassium decomposes the water, and the gold is liberated as a black powder; this is an allotropic modification of gold; it is capable of combining with water, and, when heated to dull redness, immediately assumes the ordinary golden colour.

(*b*) The alloy of iron and nickel containing 25 per cent. of nickel, when heated to 500° C. and then cooled either rapidly or slowly, has no magnetic properties, but if cooled in solid carbon dioxide it is attracted by a magnet. This magnetic change is accompanied by an increase in hardness, a decrease in electrical resistance, and a decrease in density, indicating that an allotropic change may have taken place.

48 *Segregation or Liquation in Alloys.*—During the solidification of alloys, perfect diffusion does not take place, and heterogeneous solid masses are therefore formed. Thus carbon segregates in a steel ingot, and the upper part of the axis of the ingot contains more carbon than the other portions. This is due mainly to the following causes: (1) the bottom of the ingot in contact with the cold mould is cooled more quickly than the top: (2) during cooling, the hotter portions rise and the colder portions sink: (3) the portion containing the most carbon is the last to solidify.

Another cause of segregation in alloys is the difference in the specific gravities of the different constituents; for example, in an alloy of tin and antimony, the compound SnSb, which crystallises in cubes, has a lower specific gravity than the bulk of the alloy, and when this is allowed to cool slowly, the top of

the ingot is found to be full of these cubes, and the bottom comparatively free from them. Rapid cooling through the freezing range and slow cooling afterwards tend to lessen the amount of segregation.

Diffusion of metals.—Roberts-Austen has shown that metals diffuse into other metals just in the same manner as a salt in water. Thus a ball of gold immersed in a bath of molten lead at 550° diffused into the latter at a rate more than three times as great as that of sodium chloride into water at 18°; similar results have been obtained with gold in molten bismuth and tin, silver in lead and tin, &c. Moreover, diffusion takes place even between solid metals, metallic gold contained in a cylinder of solid lead slowly diffusing into the latter even at the ordinary temperature,[1] the rate of diffusion increasing with the temperature.[2]

Physical Properties of Alloys.

49 Certain of the physical properties of the metal are always preserved in the alloy. Thus, the specific heat and the coefficient of expansion of the alloy approximate to the mean of those of its component metals, except in the case of an alloy which undergoes molecular changes during cooling. In the case of other properties such as hardness, elasticity, tensile strength, &c., a variation takes place. Thus wires of either silver, copper, tin, or zinc in the pure state are lengthened by loads which would have scarcely any effect on similar wires of their alloys, such as gun-metal and brass. Again, whilst the specific gravity of certain of the alloys is the mean of that of their constituent metals, that of others is always either greater or less than the mean specific gravity of the constituents. All alloys, with the exception of amalgams, and the alloy formed by adding one part of potassium to three of sodium, are solid at the ordinary temperature.

Conductivity of alloys.—The electrical conductivity of alloys varies with their composition, and a distinct relationship exists between the freezing point curves of the alloys and their conductivity. For example, when a series of alloys is *eutectiferous* throughout that is, when the eutectic range extends from one end of the series to the other (see line CXD, Fig. 3, p. 78) the conductivity is the mean of that of the consti-

[1] *Proc. Roy. Soc.*, 1900, **67**, 101. [2] *Nature*, 1896, **54**, 55.

tuents, as in the Sn-Zn and Sn-Pb series. In nearly all other cases the conductivity is less than the mean, and when the results are plotted in curves different types are found to exist, each type corresponding to a different group of alloys having similar freezing point curves.

The conductivity of the alloys, like that of the pure metals, decreases with rise of temperature, and *vice versa*. The increase at low temperatures is, however, not so great as with the metals.

The solubility of alloys in acids differs frequently from that of the metals forming them. If an alloy of platinum and silver is boiled with nitric acid, it is completely dissolved, whereas platinum when unalloyed is quite insoluble in this acid. On the other hand, silver by itself readily dissolves in nitric acid, but it does not do so when it is alloyed with much gold, the whole of the silver being soluble only when its quantity is at least double that of the gold. It was formerly believed that in order to separate the whole of the silver not more than one quarter of the alloy must consist of gold, whence the term *quartation*, which is still used for the separation of these metals.

Many alloys are largely employed in the arts and manufactures, as they possess properties which are wanting in the single metals. Thus, pure gold and silver are too soft to be minted, but the addition of a small proportion of copper gives them the necessary hardness. Pure copper is so soft and tenacious that it is not suitable for use in the lathe. The addition of half its weight of zinc produces the alloy brass, which is hard, and yet is sufficiently tough to be readily turned. Gun-metal is a very tenacious and hard alloy, containing nine parts of copper to one part of tin. A still harder alloy is bell-metal, consisting of two parts of tin to eight parts of copper. The more tin such an alloy contains, the lighter is its colour. Speculum metal, containing one part of tin to two parts of copper, possesses a white colour, is capable of receiving a very high polish, and is, therefore, used for the specula of telescopes. Type-metal contains various proportions of lead and antimony, generally strengthened by the addition of tin. A very good metal is composed of two parts of lead, one part of antimony, and one part of tin. This alloy is hard, easily fusible, not brittle, and it expands at the moment of solidification—properties which make it most suitable for high-class work.

Amalgams.

50 Amalgams are compounds or mixtures of metals with mercury and, although really belonging to the class of alloys, are usually distinguished by this term. The name is first found in the writings of Thomas Aquinas ; and Libavius explains the meaning of the word as follows:—"Amalgama corruptum vocabulum esse ex Graeco *μάλαγμα* non dubitant." It is perhaps more probable that the word is derived from, or through, the Arabic, as the form *algamala* also occurs in the writings of the alchemists.

The ancients were acquainted with the fact that mercury can combine with the metals, and they employed this property for the extraction of gold from its ores; Vitruvius even gives a method for extracting by means of mercury the gold from vestments which have been embroidered with gold thread. The Latin Geber speaks more distinctly respecting the compounds of the metals with mercury, for we find in his work, *Summa perfectionis magisterii*, the following words, "Mercurius adhæret tribus mineralibus de facili, Saturno (lead) scilicet, Jovi (tin) et Soli (gold). Lunæ (silver) autem magis difficulter. Veneri (copper) difficilius quam Lunæ. Marti (iron) autem nullo modo, nisi per artificium. Est enim amicabilis et metallis placabilis. Solvuntur Jupiter et Saturnus, Luna et Venus ab eo." Thus it is clear that Geber knew that, with the exception of iron, mercury combines directly with all the metals. The problem of the preparation of iron amalgam was one to which the alchemists paid great attention, as, according to Geber, it was no easy matter. Libavius gives the first hints towards the solution of this problem, as he says that the common metals require to be purified by corrosive action before they can be made to unite with mercury.

Amalgams are usually obtained by the direct union of the metal with mercury. In this case a fall of temperature is not unfrequently noticed, as when tin is dissolved in mercury. Sometimes, on the other hand, heat is evolved, as when the alkali metals are amalgamated. Amalgams are produced also by the addition of mercury to a solution of a metallic salt; thus, if mercury be added to a solution of silver nitrate, the amalgam separates out in splendid crystals—the *Arbor Dianæ* of the ancients. Another mode of obtaining an amalgam is to place the metal in a solution of mercuric nitrate, or together with

mercury and a dilute acid; and lastly, amalgams are formed by the action of a weak electric current upon a solution of a salt into which a globule of mercury has been poured, the negative pole dipping into the globule.

The amalgams correspond in their chemical relationships to alloys, consisting generally of a mixture of one or more amalgams of definite composition with an excess of mercury. The amalgams containing a large quantity of mercury are often liquid, while those which contain less are frequently found to crystallise. On squeezing the excess of mercury through chamois leather, there is obtained from liquid silver amalgam a residue of fairly uniform composition containing about 30 per cent. of silver. On similarly treating a liquid gold amalgam, a residue is obtained which contains 33 per cent. of gold. When heated above the boiling point of mercury, a number of the amalgams retain a certain proportion of mercury. Thus silver amalgam, when heated to 450°, leaves a residue which still contains 12 per cent. of mercury; and a gold amalgam treated in the same way leaves a residue containing 10 per cent. of mercury.[1] Similar results are obtained with copper, sodium, and potassium, but the metals lead, tin, cadmium, and bismuth do not retain mercury at a temperature of 450°.

On examining the various series of amalgams by the method of thermal analysis, the existence of many definite compounds has been established; thus, in the sodium amalgams,[2] the following compounds are known:

$$Hg_4Na,\ Hg_2Na,\ HgNa,\ Hg_2Na_3,\ Hg_2Na_5,\ \text{and}\ HgNa_3.$$

In a similar manner with potassium,[3] HgK, Hg_2K and Hg_9K; and with silver, Ag_3Hg_4.

Regarded as compounds, such amalgams are very unstable, for Joule [4] has shown that they can be decomposed by subjecting them to a very high pressure.[5]

Many amalgams are used in the arts. Tin amalgam is employed in the silvering of mirrors, gold and silver amalgams in the processes of gilding and silvering in the dry way; zinc and tin amalgams for coating the rubbers of electrical machines, copper

[1] De Souza, *Ber.*, 1875, **8**, 1616; 1876, **9**, 1050.
[2] Schüller, *Zeit. anorg. Chem.*, 1904, **40**, 385.
[3] Jänecke, *Zeit. physikal. Chem.*, 1907, **53**, 245.
[4] *Mem. Manch. Phil. Soc.*, 1865 (3), **2**, 115.
[5] See also Dudley, *Proc. Amer. Assoc.*, 1890, 145.

and palladium amalgam, and an amalgam of varying proportions of silver, copper, and tin, sometimes with gold and platinum, for stopping teeth.

CONSTITUTION OF SALTS, ACIDS, AND BASES.

51 The word salt even at the present day is commonly applied to sea-salt or sodium chloride, and there can be little doubt that originally the term was given to the same substance, the Greek form of the word (ἅλς) in the feminine being used for the sea itself, whereas in the masculine it denoted the solid residue left when sea-water is evaporated. The growth of the application of the word salt from a special to a generic term appears to have had its origin in the fact that just as common salt is obtained by the evaporation of sea-water, so other kinds of salt can be obtained by the evaporation of other liquids. When, for instance, wood-ashes are boiled with water, the clear solution yields on evaporation a white soluble residue to which the name of salt was applied. This extension of the term, as Kopp remarks, was, however, not accompanied by any knowledge of the chemical differences between these various soluble substances. Even up to the end of the eighteenth century this wide application of the word salt may be said to have been prevalent.

Amongst the alchemistic writings of the earliest times the words salpetræ, salnitri, salmarinum, salarmoniacum, salvegetabile and the like, occur; these bodies are all soluble in water, and may be obtained again from solution by evaporation. The ideas connected with these salts were vague and indefinite. But a new meaning was afterwards given to the word salt, the term being applied to the solid bodies obtained by the combustion or ignition of substances. This view was upheld by Paracelsus, and was generally, though not universally, adopted by chemists. Thus we find in the seventeenth century that salt was considered to be one of the hypothetical essential constituents of all bodies, every substance being made up of salt, sulphur, and mercury (see Historical Introduction, Vol. I., p. 7). The view that salt is an essential constituent of all bodies was strongly opposed by Boyle, who paid much attention to the investigation of salts, and to whom we owe much of our knowledge of the special nature of the

different salts. He did not, however, define exactly to what class of bodies the term salt ought to be applied. This was specially accomplished by Boerhaave, who, in his *Elementa Chemiæ*, published in 1732, describes the special characteristics of salts to be their solubility, fusibility, volatility, and taste, alkalis and acids being, according to this definition, also considered as salts. These were divided into salia alcalina, salia acida, salia salsa, salia media, salia neutra, and salia composita. Under the last named was understood a class of salts obtained by the union of an acid with an alkali or metallic calx. The chief characteristics of the salts still remained their solubility and peculiar taste. It was soon seen that such a definition led to contradictions, for baryta, nitric acid, and sulphuric acid would thus be salts as well as nitrate of barium, whilst sulphate of barium, which is insoluble, and, therefore, possesses no taste, would not be a salt. Hence the necessity became obvious of separating alkalis and acids from the true salts, or salia media as they were called, and the word salt was then taken to mean such substances as are obtained when an acid and a base are brought together, or when an alkali or metallic calx is neutralised by an acid.

52 Although acids and alkalis were included among the salts, chemists had long recognised that these substances were characterised by special properties. The only acid known to the ancients was vinegar or acetic acid. Hence the name of this substance and the notion of acidity were represented by closely-related words (ὄξος, *acetum*, vinegar; ὀξύς, *acidus*, acid). The effervescence produced when vinegar is added to the carbonate of an alkali was observed in early times: thus we read in Proverbs xxv. 20, "As he that taketh away a garment in cold weather, and as vinegar upon nitre, so is he that singeth songs to a heavy heart." Nitre in this case stands for natron or native carbonate of soda. It was also well known that vinegar acted as a solvent upon many substances, as in the celebrated story of Cleopatra dissolving pearls. The Arabians were acquainted with many other acids. The Latin Geber termed nitric acid *aqua dissolitiva*, and he gave the same name to the liquid obtained by strongly heating alum in a retort, which was probably dilute sulphuric acid. This shows that the special characteristic of an acid, according to the older alchemists, was its power of dissolving substances which are insoluble in water.

Other properties common to the whole class of acids were

not observed until a much later date. In 1668 Tachenius noticed that all acids are capable of combining with alkalis, and he therefore considered silica to be an acid. Boyle[1] points out that the substances known as acids have the following properties. They are bodies which (1) act as solvents, but act with varying power on different bodies; (2) precipitate sulphur and other bodies from their solutions in alkalis; (3) turn blue vegetable colouring matter red, whilst alkalis bring the blue colour back again; (4) can combine with alkalis, when the characteristic properties of each body disappear and a neutral salt is formed. The properties just enumerated were henceforward regarded as the special characteristics of acids, and accordingly F. Hofmann, in 1723, asserted that the *spiritus mineralis*, which exists in many mineral springs, and which we term carbonic acid, belongs to the class of acids since it turns blue litmus solution red. Thirty years later Black strengthened this conclusion by showing that this same substance possesses the power of destroying the caustic nature of the alkalis, giving rise to a distinct class of salts.

53 Such alkaline substances as lime, the potashes obtained by the combustion of plants or by heating cream of tartar, and natron, or native carbonate of soda, were well known to the Greeks, Hebrews, and Romans, whilst the spirit of urine became known to the alchemists of the thirteenth century. These substances, however, were not generally looked upon as possessing the common property of alkalinity until the time of the iatrochemists, who ascribed the various diseases of the body to changes in the relative proportions of acid and alkali in the various organs and fluids, and indeed sought to explain all chemical phenomena as action between acids and alkalis. Some of the special characteristics of alkalis which were recognised about this time have already been mentioned in discussing the properties of the acids, and to these was added the power of effervescing with acids. The caustic alkalis which did not effervesce with acids were supposed to be more complex than the mild alkalis. Thus lime was supposed to acquire its caustic properties by taking up igneous particles from the fire in which the limestone was burned; when it was added to a mild alkali, these particles passed into the latter and

[1] *Reflections upon the Hypothesis of Alcali and Acidum*, **4**, 284, and elsewhere.

rendered it caustic. This belief endured until Black in 1755 discovered the true nature of the phenomenon. The alkalis known at about the middle of the eighteenth century were the volatile alkali, and the two fixed alkalis, distinguished as the mineral alkali (soda), and the vegetable alkali (potash).

54 In the new system of chemistry founded by Lavoisier after the overthrow of the phlogistic theory (*see* Vol. I., pp. 25–32), the three classes of substances, acids, bases, and salts were for the first time clearly separated. The acids, distinguished by the properties already discussed, comprised the compounds of certain elements (the acidifiable bases) with oxygen, whilst the alkalis, earths, and metallic oxides possessed the common property of being able to combine with acids to form the third class of substances, the salts, in which the properties of alkalinity and acidity were alike wanting. The discovery of the compound nature of the alkalis by Davy (1807) justified Lavoisier's classification, inasmuch as these substances were thereby proved to be metallic oxides.

The view that all acids contain oxygen—a view to which this element owes its name—was soon adopted generally. On the other hand, it was pointed out by Berthollet that prussic acid and sulphuretted hydrogen, which do not contain oxygen, acted in many respects as acid bodies. Lavoisier's views, however, carried the day, it being assumed that the substances just mentioned really contained oxygen. The next step in the progress of our knowledge on this subject was Davy's investigations on chlorine and hydrochloric acid (1808–1810), which proved the existence of a powerful acid not containing oxygen. Gay-Lussac's discovery of hydriodic acid, and the proof that prussic acid likewise contains no oxygen (1815), soon supplied further evidence of the same kind. Acids were henceforth divided into two classes, the *oxyacids* and the *hydracids*, whilst the salts derived from them were known as *amphid* salts (*ἀμφί*, both, since the acid radical and the base both contained oxygen), and *haloid* salts (*ἅλς*, sea-salt, *εἶδος*, like) respectively. The sulphides and selenides were afterwards included among the amphid salts because of the analogy of sulphur and selenium with oxygen. These elements were for this reason termed amphids, whilst the elements of the chlorine group, which combine directly with metals to form haloid salts, were termed haloids. The oxyacids were the substances which we now term the acid-forming oxides, whilst those bodies which we now term

the oxygenated acids were considered to be the hydrates of these oxyacids.

The dualistic view that salts are formed either by the union of an acid with a metallic oxide, sulphide, or selenide, or by the direct union of a metal with a haloid element, received its most complete expression in the electrochemical theory of Berzelius.

The fundamental principle of this system was laid down by its author in the statement that "in every chemical combination there is a neutralisation of opposite electricities, and that this neutralisation produces heat in the same manner as it is produced by the discharge of a Leyden jar, without being in this latter case accompanied by an act of chemical combination." The application of this principle led to the view that "every compound substance, whatever the number of its constituent principles, may be divided into two parts, one of which is electrically positive towards the other. For example, sulphate of soda is not compounded of sodium, oxygen, and sulphur, but of sulphuric acid and soda, each of which can again be divided into two elements, one positive, the other negative. In the same way alum cannot be regarded as directly compounded of its simple principles; it must rather be considered as the product of the reaction of sulphate of alumina, the negative element, on sulphate of potash, the positive element."[1] In accordance with this theory Berzelius wrote the formula for sodium sulphate $NaO+SO_3$, or in his contracted formulæ $\dot{N}a\ddot{S}$.

The amphid salts were thus looked upon as compounds of the second order, formed by the union of two oxides, each of which was a compound of the first order, formed from its elements. The haloid salts, on the other hand, such as KCl, were compounds of the first order.

55 At this time no distinction was made between what are now known as mono-, di-, and tri-basic acids. Thus nitrate of potash was supposed to be formed in a precisely similar manner to the sulphate, and the formulæ of these two salts were accordingly written by Berzelius, $KO.N_2O_5$, and $KO.SO_3$, the atomic weight which was then adopted for potassium being twice that now in use. When two salts of the same acid and base were known, such as the sulphate and bisulphate of potash, it was supposed that the second salt was formed by the combination of the first with the second molecule of the

[1] Berzelius, *Traité de Chimie.*

acid; the formula of the second salt was therefore written $KO.SO_3 + H_2O.SO_3$, or $KO.2SO_3$, the water being sometimes omitted.

The researches on the phosphates carried out by Graham in 1833 showed that this theory must be modified, since, if trisodium phosphate contained only one atom of base, the formula of phosphoric acid would become $P_{\frac{2}{3}}O_{\frac{5}{3}}$, which was incompatible with the atomic weights of phosphorus and oxygen, as determined independently. Graham showed that the formation of the ortho-phosphates might be readily explained by supposing that phosphoric acid was capable of combining with three atoms of base, and that this base might be either water or a metallic oxide. He therefore formulated orthophosphoric acid and its sodium salts as follows (the modern equivalents of his formulæ being employed):

Orthophosphoric acid . .	$P_2O_5 + 3H_2O$.
Acid sodium phosphate . .	$P_2O_5 + 2H_2O + Na_2O$.
Ordinary sodium phosphate	$P_2O_5 + H_2O + 2Na_2O$.
Trisodium phosphate . .	$P_2O_5 + 3Na_2O$.

The water in the first, second, and third of these salts is essential to the composition of the salt, since when it is removed new salts are formed (Vol. I., p. 656).

In 1838 Liebig published his important investigation on the constitution of the organic acids, in which he showed that many of these resembled phosphoric acid in their relations to bases. He further proposed that all acids which formed mixed salts containing two different, non-isomorphous bases, should be considered as belonging to the same class as phosphoric acid. In this memoir, moreover, he discussed the question whether the salts and oxyacids are compounds of a metallic oxide or water with an acid-oxide, or whether all salts and acids may be represented as combinations of metals or hydrogen with some other element or group of elements. This view had been originally suggested by Davy, and independently by Dulong (in 1816), but had not been generally accepted. The difference in constitution between the oxyacids and the hydracids necessitated a different explanation for reactions which are in fact similar. Thus, for instance, it was assumed that when hydrochloric acid acted upon zinc the metal simply replaced the hydrogen of the acid:

$$Zn + 2HCl = H_2 + ZnCl_2.$$

In the action, however, of sulphuric acid upon zinc it was necessary to assume that the presence of the acid enabled the zinc to decompose the water (predisposing affinity) in order that an oxide might be formed with which the acid could unite; the reaction was, accordingly, represented as taking place in two stages:

$$(1)\ Zn + H_2O = H_2 + ZnO$$
$$(2)\ SO_3 + ZnO = SO_3,ZnO.$$

Similarly, when hydrochloric acid reacts with lime, water is formed, whilst, when the same base combines with sulphuric acid, no water is produced:

$$(1)\ 2HCl + CaO = H_2O + CaCl_2.$$
$$(2)\ SO_3 + CaO = SO_3,CaO.$$

Liebig pointed out that the new view does away with these inconsistencies and also with the distinction between hydracids and oxyacids, amphid salts and haloid salts; acids are simply hydrogen compounds, the hydrogen in which can be replaced by metals, so giving rise to salts. In Liebig's opinion this view is less applicable to inorganic than to organic compounds. The analogous constitution of acids and salts was, however, not generally admitted until certain facts became known which were favourable to this theory.

56 If aqueous hydrochloric acid is decomposed by an electric current between platinum electrodes, chlorine is evolved at the positive and hydrogen at the negative pole respectively. If dilute sulphuric acid is treated in a similar way, a simple decomposition of water apparently takes place, for at the positive pole we obtain only oxygen and at the negative pure hydrogen. The same phenomenon is observed in the electrolytic decomposition of a solution of sodium sulphate, but, in addition, sulphuric acid is produced at the positive pole, and soda at the negative pole. Hence it was argued that in this case, the current decomposed both the water into its elements, and the salt into its immediate components. If a solution of sulphate of copper is subjected to the same treatment, oxygen is evolved and sulphuric acid is produced at the positive pole, whilst at the negative pole metallic copper separates out; this was explained by the supposition that the copper oxide which ought to be deposited is reduced to the condition of metal by the nascent hydrogen.

These phenomena were specially examined by Daniell.[1] It appeared to him important to determine the relation between the quantities of oxygen and hydrogen, on the one hand, and of the acid and the alkali on the other, formed in the electrolysis of a salt of an alkali. As the result of a large number of careful experiments, he found that these several substances are produced in the proportion of their equivalents, and that this is true not only with sodium sulphate, but also with other salts of the alkalis. Daniell recorded also the remarkable fact that the same current which apparently is capable of producing these two decompositions is capable of liberating exactly the same quantities of hydrogen and of oxygen from dilute sulphuric acid. In the latter case, the current is apparently able to effect only half the work which it can do in the electrolysis of an aqueous saline solution, because in the latter case not only the salt but, as it seems, the water also, undergoes decomposition. This is, however, clearly impossible, and the phenomena observed can be readily explained by assuming that in the decomposition both of aqueous sulphuric acid, and of the solution of a sulphate, either hydrogen or a metal is liberated at the negative pole, whilst at the positive pole the group SO_4 is set free. But this group cannot exist in the free condition, and decomposes at once into oxygen and sulphur trioxide, the latter dissolving instantly to form sulphuric acid. When a salt of an alkali is electrolysed, the metal which is liberated instantly decomposes the water with evolution of hydrogen. According to this view, the electrolytic decomposition of the oxysalts is exactly analogous to that of the chlorides, and hence they must be similarly constituted. Daniell proposed a new nomenclature for the oxysalts:

H_2SO_4	Hydrogen oxysulfion,
Na_2SO_4	Sodium oxysulfion,
HNO_3	Hydrogen oxynitrion, &c.,

which, however, has never been generally adopted.

The further development of chemical theory has completely confirmed the view that acids and salts are strictly analogous, salts being derived from acids by the replacement of hydrogen by a metal. This analogy has received expression in the nomenclature employed by many chemists for these substances, according to which the acids are termed hydrogen salts. Thus, just as nitre

[1] *Introduction to Chemical Philosophy*, second edition (1843), p. 533.

is called potassium nitrate, nitric acid is called hydrogen nitrate, sulphuric acid hydrogen sulphate, &c. In 1851 Williamson pointed out that the basic oxides and hydroxides, the oxygen acids and their salts, might all be considered as derived from one or more molecules of water, by the partial or complete replacement of the hydrogen by other elements or groups. When the hydrogen of water is replaced by a metal, a basic oxide or hydroxide is produced, so that caustic potash and oxide of potassium have the formulæ $\frac{K}{H}O$ and $\frac{K}{K}O$. When, on the other hand, the hydrogen is partially replaced by chlorine, or a group of atoms such as NO_2, ClO_3, SO_2, &c., acids are formed, viz.:— $\frac{NO_2}{H}O$, $\frac{(ClO_3)}{H}O$, $\frac{SO_2}{H_2}O_2$, &c., the hydrogen of which can be replaced by metals with the formation of salts.[1]

57 If we ask ourselves the question, What is the cause of the acid character of bodies? we may say that acids must contain hydrogen together with certain elements or groups of elements which are termed negative elements or groups, inasmuch as these separate out at the positive pole in the process of electrolysis. A compound may, however, contain these negative elements or groups of elements, and also hydrogen, and yet not belong to the class of acids. Hence it appears that the atoms or groups of atoms must be combined with hydrogen according to a particular plan in order that the compound may assume the character of an acid. Sir Humphry Davy,[2] in 1816, pointed out perfectly correctly that it is impossible to assert that a particular body is an acid-forming or an alkali-forming principle, and that such a definition would be nothing more than to re-introduce *qualitates occultas* into science. The chemical properties of a body, said Davy, are determined by "the corpuscular arrangement" of the constituent particles.

Amongst the different acids, the hydrogen compounds of the elements of the chlorine group possess the simplest constitution. They contain one atom of hydrogen combined with one atom of a powerful negative element. In the oxygen acids the hydrogen which can be replaced by metals is always found to be combined with oxygen in the form of the radical hydroxyl, OH; this is proved by the fact that these acids can as a rule be

[1] *Journ. Chem. Soc.*, 1852, **4**, 350.
[2] *Jour. Sc. and Arts, Roy. Inst.*, 1816.

obtained by the action of water on the corresponding chlorides:

$$SO_2\begin{matrix}Cl\\Cl\end{matrix} + 2H_2O = SO_2\begin{matrix}OH\\OH\end{matrix} + 2HCl.$$

The ease with which the hydrogen of such a hydroxyl group can be replaced by a metal depends upon the nature of the group with which it is combined. This is well illustrated by many organic compounds, which assist us more than any other class in the solution of the problem as to what determines the acid nature of a compound. From a study of the organic acids it appears that when the OH group is combined with the group CO, the compound containing these groups is an acid, whilst when the OH group is united with the groups CH_2 or CH_3 the compound is not an acid. Thus formic and acetic acids are monobasic acids, malonic and oxalic are dibasic acids:

$\begin{matrix}H\\\vert\\CO.OH\end{matrix}$	$\begin{matrix}CH_3\\\vert\\CO.OH\end{matrix}$	$\begin{matrix}CO.OH\\\vert\\CO.OH\end{matrix}$	$CH_2\begin{matrix}CO.OH\\CO.OH\end{matrix}$
Formic acid.	Acetic acid.	Oxalic acid.	Malonic acid.

whilst alcohol, $CH_3.CH_2.OH$, is not an acid; hydroxy-acetic acid, which contains two OH groups, is nevertheless monobasic, and tartaric acid, which contains four OH groups, is only dibasic:

$\begin{matrix}CH_3\\\vert\\CH_2.OH\end{matrix}$	$\begin{matrix}CH_2.OH\\\vert\\CO.OH\end{matrix}$	$\begin{matrix}CH(OH).CO.OH\\\vert\\CH(OH).CO.OH\end{matrix}$
Alcohol.	Hydroxy-acetic acid.	Tartaric acid.

The group SO_2 exerts a similar influence, so that such a substance as $C_6H_5.SO_2.OH$ is also found to be an acid.

Although it is characteristic of all acids that they contain hydrogen which can be replaced by metals, some substances which fulfil this condition are not acids. Thus compounds of such different properties as ammonia, NH_3, water, H_2O, and alcohol, C_2H_5OH, all yield metallic derivatives, NH_2Na, NaOH, and C_2H_5ONa, when they are directly acted on by metallic sodium; whilst marsh gas, CH_4, and benzene, C_6H_6, can by indirect means be converted into organo-metallic derivatives such as $(CH_3)_2Zn$ and $(C_6H_5)_2Hg$. It is therefore usual to define acids as compounds which contain hydrogen capable of being

replaced by a metal when the latter is presented to them in the form of a hydroxide. It is, however, impossible to draw a hard and fast line between substances which are, and those which are not acids, since, especially among the organic compounds, the two classes pass imperceptibly into one another.

Constitution of Salts, Acids, and Bases in Dilute Solution.

58 As already explained (Vol. I., pp. 122—126), the behaviour of acids, bases, and salts in dilute solution has led to the conclusion that these substances are dissociated into equal quantities of positively charged ions, or kations, and negatively charged ions, or anions, the extent of dissociation increasing in all cases with the dilution of the solution. Acid properties are found to be peculiar to substances which yield hydrogen as a kation, whilst the anion OH is characteristic of basic substances. Weak acids and bases, such as acetic acid, boric acid, ammonia, &c., are found to be only very slightly dissociated, whilst strong acids and bases, such as hydrochloric and nitric acids, caustic soda, and caustic potash, are very largely dissociated even in moderately strong solution. The percentage of dissociated molecules in solutions which contain 1 gram equivalent per litre of the various substances, is about 80 for the strongest acids and bases, and 0—10 for weak acids and bases. Salts which yield a univalent kation and a univalent anion are dissociated, at the afore-mentioned concentration, to the extent of 60—70 per cent., even when the acid and base from which the salt is derived are both weak.

The action of acids, bases, and salts on the colouring matters known as indicators, such as litmus, phenolphthalein, &c., receives a very interesting explanation in the light of this theory. The substances which are used as indicators are themselves either weak acids, or weak bases, or salts derived from them. Thus blue litmus solution contains the sodium salt of a very weak acid, the ions being the colourless kation $\overset{+}{\mathrm{N}}\mathrm{a}$, and a complex anion which gives the liquid its blue colour. When an acid is added to the solution these complex anions are brought into the presence of free hydrogen ions, with which they immediately unite to form molecules of the weak acid of litmus. This is much less dissociated than its sodium

salt, and causes the liquid to appear red, the change of colour being due to the fact that the molecule of the undissociated acid has a different colour from that of the anion.

It follows from the above that an acid indicator will be sensitive only to acids which are much more strongly dissociated than itself, since only such acids will bring about the practically complete removal of the anions of the litmus acid by combination with hydrogen ions. Hence it is that the various indicators differ in their sensibility towards acids, and that some weak acids such as boric acid do not show an acid reaction towards litmus. In the same way, methyl-orange is not affected by carbonic acid or by sulphuretted hydrogen; properties of which advantage is taken in various methods of volumetric analysis. Similar considerations hold with regard to the reactions of basic substances. Thus, when caustic soda is added to a solution of red litmus, the few free hydrogen ions of the litmus acid unite with the $\overset{-}{OH}$ anions of the caustic soda, forming water. Equilibrium being thus disturbed, fresh molecules of the acid undergo dissociation; the hydrogen ions thus liberated unite with the $\overset{-}{OH}$ anions, and this process goes on until practically the whole of the molecules of the acid have been dissociated; the corresponding number of molecules of water are formed, and the solution finally contains kations of $\overset{+}{Na}$, the $\overset{-}{OH}$ anions from the excess of caustic soda, and the anions of the litmus acid, which render the liquid blue.[1]

Molecules capable of yielding more than two ions appear to be only very partially dissociated even at fairly low concentrations. Thus, for example, sulphuric acid, which is capable of yielding the three ions $\overset{+}{H}$, $\overset{+}{H}$, $\overset{--}{SO_4}$, is found in dilute solutions to be mainly dissociated into the two ions $\overset{+}{H}$, and $\overset{-}{HSO_4}$, whilst only a comparatively small proportion of the $\overset{-}{HSO_4}$ ions are further dissociated into $\overset{+}{H}$ and $\overset{--}{SO_4}$. The second stage of the dissociation does not become very prominent until concentrations of the order of one-tenth or one-hundredth of a gram equivalent per litre are reached.

Some salts in which no replaceable hydrogen is present do not give a neutral reaction when dissolved in water, whilst others

[1] For this and other theories of indicators, see Thiel, Ahrens' Sammlung, 1911, **16**, 307.

containing replaceable hydrogen are not acid to indicators. Thus salts formed from a strong acid and a weak base, such as ferric chloride, chromic chloride, aluminium sulphate, &c., usually have an acid reaction, whilst, on the other hand, salts formed from a weak acid and a strong base have an alkaline reaction, as is seen in the case of sodium carbonate, sodium borate, sodium nitrite, sodium aluminate, sodium silicate, &c. Moreover, disodium hydrogen phosphate, Na_2HPO_4, sodium bicarbonate, $NaHCO_3$, and similar acid salts are neutral, or even alkaline, to indicators. It seems probable that in such cases the salt is partially decomposed or hydrolysed by the solvent water, which, as shown by its electrical conductivity, contains a certain number of free hydrogen and hydroxyl ions, although this number must be a very small one (Vol. I., p. 300). Taking the example of a salt of a weak monobasic acid, such as nitrous acid, with a strong base, such as caustic soda, we have the following relations. When sodium nitrite is dissolved in water the following reaction probably occurs between a few of the ions of the salt and the free ions $\overset{+}{H}$ and $\overset{-}{OH}$, to which reference has just been made, molecules of the weak, slightly dissociated acid, HNO_2, being formed:

$$\overset{+}{Na} + \overset{-}{NO_2} + \overset{+}{H} + \overset{-}{OH} = \overset{+}{Na} + \overset{-}{OH} + HNO_2.$$

As a result of this action there remains an excess of hydroxyl ions, and the solution has therefore an alkaline reaction. Similar conditions prevail in solutions of many salts of weak acids, for example, those of potassium cyanide, which always smell of hydrogen cyanide. When, on the other hand, the salt has been formed from a strong acid and a weak base, the hydrogen ions are present in excess, and the solution has an acid reaction. Some salts which have been formed from a weak acid and a weak base are completely decomposed in dilute solution. This is especially characteristic of the salts of the weak organic bases.[1]

METALLIC OXIDES, HYDROXIDES, AND SALTS.

59 All the metals combine with oxygen. Some, such as those of the alkalis and alkaline earths, unite with oxygen so readily

[1] *See* Ostwald, *The Scientific Foundations of Analytical Chemistry.* Translated by McGowan (Macmillan, 1900).

that they have to be preserved out of contact with air. Other metals withstand the action of oxygen at the ordinary temperature, but combine with it when heated. When such metals are easily volatile, as is the case with magnesium and zinc, they burn with a bright flame in the air or in oxygen. If they do not volatilise readily, *e.g.*, tin and lead, the metals gradually undergo oxidation without production of light. A few metals, such as gold and platinum, cannot be made to unite directly with oxygen, even at the highest temperatures, but their oxides can be prepared by indirect means. Chlorine attacks all metals, and if the chlorides of those metals which are not directly oxidisable are decomposed by an alkali, their oxides or hydroxides are formed: thus—

$$2AuCl + 2KOH = Au_2O + 2KCl + H_2O.$$

Representatives of each of the three classes—basic oxides, peroxides, and acid-forming oxides—into which the oxides in general may be roughly divided (Vol. I., p. 260), are found among the oxides of the metals.

(a) *Basic Oxides.*—The term basic oxide is applied only to such oxides as react with acids to form the corresponding salt and water, and hence all these oxides are formulated as derived from water by the replacement of hydrogen by a metal, or a radical containing a metal united with oxygen. Thus in uranium oxide, UO_3, which yields salts such as $UO_2(NO_3)_2$, the hydrogen of water is replaced by the radical UO_2, which is present also in the salts. When only a part of the hydrogen is replaced by a metal or radical, the resulting compound is termed a hydroxide, *e.g.*, $Ca(OH)_2$. The hydroxides were formerly called hydrates, as they were supposed to be compounds of the oxides with water.

Many of the metals form several basic oxides and corresponding series of salts, in which they have a different equivalent, as shown in the following list:

Mercurous oxide .	Hg_2O	Mercuric oxide . .	$Hg=O$
Ferrous oxide . .	$Fe=O$	Ferric oxide .	Fe_2O_3
Ferrous hydroxide .	$Fe(OH)_2$	Ferric hydroxide .	$Fe(OH)_3$

It must be remembered that only the empirical formula of most of the oxides and hydroxides is known, and that therefore no conclusion as to the valency of the metal can be drawn from these formulæ. Thus ferrous oxide may, for all we know, have the formula Fe_2O_2, and the constitution $O=Fe—Fe=O$.

The basic oxides are, as a rule, obtained by the direct oxidation of the metal, or by one of the following methods:

(1) The decomposition by heat of a salt derived from the metal and an acid the anhydride of which is volatile, or yields volatile decomposition products:

$$PbCO_3 = PbO + CO_2.$$
$$ZnSO_4 = ZnO + SO_3.$$
$$4Al(NO_3)_3 = 2Al_2O_3 + 12NO_2 + 3O_2.$$

(2) The decomposition of the hydroxide by heat:

$$2Cr(OH)_3 = Cr_2O_3 + 3H_2O.$$

The basic hydroxides are usually prepared as follows:

(1) By the reaction of a soluble hydroxide on a salt of the metal:

$$2NaHO + ZnSO_4 = Na_2SO_4 + Zn(OH)_2.$$

The oxide itself is, however, sometimes formed in this reaction instead of the hydroxide:

$$2NaOH + 2AgNO_3 = 2NaNO_3 + Ag_2O + H_2O.$$

(2) By the direct combination of the oxide with water:

$$CaO + H_2O = Ca(OH)_2.$$

The hydroxides of the alkali metals are the most soluble. They are termed *alkalis*, and are distinguished by their caustic taste. The hydroxides of the metals of the alkaline earths are less soluble. Most of the other hydroxides and basic oxides are almost insoluble in water. Exceptions to this are thallous hydroxide, which is very soluble in water, and the oxides of lead, silver, and magnesium, which dissolve very slightly.

(b) *Acid-forming Oxides.*—The hydroxides corresponding with these oxides are the acids, but only comparatively few of these are known in the free state among the derivatives of the metals. Like the basic oxides, they are formulated as derived from water by the complete or partial replacement of the hydrogen by a

metal or radical. They are usually obtained by the addition of a stronger acid to a salt derived from the acid-forming oxide in question:

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + 2CrO_3 + H_2O.$$

It is a general rule that the acid-forming oxides of a metal contain more oxygen than the basic oxides of the same metal. Thus Bi_2O_3 is a basic oxide, while Bi_2O_5 is a weak acid-forming oxide; again, VO is a basic oxide, whilst V_2O_5 yields a strong acid which forms stable salts.

(c) *Peroxides.*—The term peroxide is applied generally to oxides which are neither basic nor acid-forming, but contain more oxygen than the basic oxides of the same metal. Many of these peroxides appear to be derived from hydrogen peroxide in the same way as the basic and acid-forming oxides are derived from water. Thus, when they are treated with an acid they yield a salt and hydrogen peroxide:

$$Ba\begin{matrix}O\\|\\O\end{matrix} + 2HCl = BaCl_2 + H.O.O.H,$$

while some of them may be prepared by double decomposition between a salt of the metal and hydrogen peroxide. In some cases such oxides are to be considered as having a mixed constitution, part of their oxygen being derived from water and part from hydrogen peroxide.

Peroxides which are not true derivatives of hydrogen peroxide, on the other hand, act in the presence of acids simply as oxidising agents. Thus, when they are treated with hydrochloric acid, chlorine is evolved, and the salt corresponding to a lower basic oxide is formed:

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

It is, however, impossible to employ this reaction as the basis of a rigid classification of the peroxides, since the behaviour of the various oxides towards hydrochloric acid has not been sufficiently investigated.

This action of hydrochloric acid on the higher oxides of the metals is frequently employed for the determination of the composition of these oxides, and for their analytical estimation (Bunsen). The chlorine evolved from a known weight of the oxide is passed into a solution of potassium iodide, and the

iodine liberated is estimated by means of a standard solution of sodium thiosulphate. Many oxides which are not peroxides undergo the same reaction, a salt corresponding with a lower oxide being formed:

$$2CrO_3 + 12HCl = 6H_2O + 2CrCl_3 + 3Cl_2.$$

60 In addition to the classes of oxides which have already been discussed, many metals also yield *sub-oxides*, containing less oxygen than the lowest oxide of the metal which is capable of yielding salts, *e.g.* Cu_4O, Pb_2O, &c. The constitution of these oxides is not at present understood. Many metals, moreover, form *intermediate oxides*, to which no corresponding salts are known. Such oxides are intermediate in composition between two of the other oxides of the metal, and generally yield a mixture of products when treated with acids. Thus magnetic oxide of iron, Fe_3O_4, which is intermediate between ferrous and ferric oxides, FeO and Fe_2O_3, yields a mixture of ferrous and ferric chlorides when it is dissolved in hydrochloric acid:

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Red lead, Pb_3O_4, on the other hand, which is intermediate between the monoxide and the peroxide of lead, PbO and PbO_2, is converted into lead nitrate and lead peroxide when it is treated with dilute nitric acid:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

61 It will be seen from the foregoing that the classification of the oxides is based mainly on the behaviour of these compounds with regard to the formation of salts. Since an oxide may exhibit varying behaviour in this respect when it is placed under different conditions, it follows that the same oxide may be found as a member of more than one class. Many oxides, for example, act as basic oxides towards strong acids, but as acid-forming oxides towards strong bases, and on this ground are described as "amphoteric." Thus aluminium hydroxide is dissolved by sulphuric acid with formation of aluminium sulphate:

$$2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O,$$

and also by caustic soda with formation of sodium aluminate,

$$Al(OH)_3 + NaOH = Al(OH)_2ONa + H_2O.$$

Again, when black oxide of manganese, MnO_2, is warmed with

hydrochloric acid, chlorine is evolved and manganous chloride is formed, so that the oxide behaves as a peroxide:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

At a lower temperature, however, an unstable salt is formed which is known only in solution, so that in this case the oxide acts as a basic one:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

The same oxide combines also with strongly basic oxides such as lime, CaO, to form unstable manganites, such as $CaO.MnO_2$, in which it plays the part of an acid-forming oxide.

62 Salts may be divided into several groups.

(1) *Normal salts* are those in which the whole of the replaceable hydrogen of an acid is completely replaced by a metal. These were formerly called *neutral salts*, or *salia media*, because it was noticed that when an alkali was added in the right proportion to a powerful acid the resulting salt possessed neither an alkaline nor an acid reaction. This, however, is not the case with every normal salt (see p. 102).

Polybasic acids can form salts containing two or more different metals: as, for instance, potassium sodium carbonate, $CO\begin{cases}OK\\ONa\end{cases}$. Polyacid bases, on the other hand, may give rise to salts which contain two acid radicals: *e.g.*, $Sr\begin{cases}ONO_2\\OC_2H_3O\end{cases}$, a compound which is at the same time a nitrate and an acetate; as another and more complex example the mineral vanadinite may be cited, $VO\begin{cases}O\\O\\OCaCl\end{cases}Ca$, which is a calcium salt of tribasic vanadic acid, and at the same time a chloride.

The salts formed by the union of an acid-forming oxide with a normal salt, or by the removal of water from an acid salt, are sometimes called acid salts, but are really normal salts derived from complex acids, which, however, often do not exist in the free state. Sodium pyrophosphate, for instance, which is obtained by heating ordinary sodium phosphate to redness,

$$\begin{matrix}PO\begin{cases}(ONa)_2\\OH\end{cases}\\PO\begin{cases}OH\\(ONa)_2\end{cases}\end{matrix} = \begin{matrix}PO\begin{cases}(ONa)_2\\O\\(ONa)_2\end{cases}\end{matrix} + H_2O,$$

is the normal salt of pyrophosphoric acid, $H_4P_2O_7$, which can be prepared in the free state, and also yields an acid salt, $Na_2H_2P_2O_7$. The acids corresponding with potassium dichromate, $K_2Cr_2O_7$, borax, $Na_2B_4O_7$, &c., on the other hand, are not known. Further examples of this class of substances are potassium disulphate or pyrosulphate, obtained by heating potassium hydrogen sulphate,

$$SO_2\begin{cases}OK\\OH\end{cases} \quad SO_2\begin{cases}OK\\O\end{cases} \quad + \quad H_2O,$$
$$SO_2\begin{cases}OH\\OK\end{cases} = \quad SO_2\begin{cases}O\\OK\end{cases}$$

sodium metabisulphite, $Na_2S_2O_5$, and many complex phosphates borates, and silicates (Vol. I., pp. 665, 729, 917).

(2) *Acid salts* are formed when only a portion of the replaceable hydrogen contained in a polybasic acid is substituted by a metal. The acid salts often possess an acid reaction, as is the case with acid potassium sulphate, $SO_2\begin{cases}OK\\OH\end{cases}$, but, as we have seen, this reaction is dependent on the nature of the acid and the base (see p. 102).

(3) *Basic salts* stand in the same relation to the basic hydroxides as the acid salts to the acids. They may be regarded as formed from the basic hydroxides by the reaction of only a part of their hydroxyl groups with the hydrogen of an acid, *e.g.* $Zn\begin{cases}OH\\Cl\end{cases}$.

Some of these salts do not contain a hydroxyl group, and these may be considered as the normal salts of complex basic radicals. Thus, basic bismuth chloride (bismuth oxychloride), BiOCl, may be looked upon as the chloride of BiO(OH), derived by loss of water from bismuth hydroxide, $Bi(OH)_3$, just as metaphosphoric acid is derived from ortho-phosphoric acid.

Basic salts are sometimes formed by the combination of a normal salt with a hydroxide. Thus, if a solution of lead nitrate is boiled with lead hydroxide, a basic lead nitrate is formed:

$$Pb\begin{cases}ONO_2\\ONO_2\end{cases} + Pb\begin{cases}OH\\OH\end{cases} = 2Pb\begin{cases}OH\\ONO_2.\end{cases}$$

Basic zinc chloride, $Zn\begin{cases}Cl\\OH,\end{cases}$ may be obtained in the same way.

Basic bismuth nitrate, on the other hand, is obtained by the action of water on the normal salt:

$$Bi\begin{cases}ONO_2\\ONO_2\\ONO_2\end{cases} + 2H_2O = Bi\begin{cases}OH\\OH\\ONO_2\end{cases} + 2NO_2OH.$$

Amongst other basic salts may be mentioned:

Malachite. Blue Carbonate of Copper. White Lead.

$$CO\begin{cases}OCuOH\\OCuOH\end{cases} \qquad CO\begin{cases}OCuOH\\O\end{cases}Cu \qquad CO\begin{cases}OPbOH\\O\end{cases}Pb$$
$$CO\begin{cases}O\\OCuOH\end{cases} \qquad CO\begin{cases}O\\OPbOH.\end{cases}$$

Basic Mercuric Sulphate.

$$SO_2\begin{cases}OHgO\\OHgO\end{cases}Hg.$$

(4) *Complex and Double Salts.* When two salts are dissolved in water and the solution evaporated, it frequently happens that the crystals which are formed contain the two salts combined in definite molecular proportions, often along with water of crystallisation. Thus, when potassium sulphate, K_2SO_4, and aluminium sulphate, $Al_2(SO_4)_3,18H_2O$, are treated in this way, crystals of potash alum, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, are obtained; whilst potassium chloride, KCl, and platinic chloride, $PtCl_4$, yield the compound K_2PtCl_6, potassium platinichloride. A distinction is usually made between complex salts such as potassium platinichloride, and double salts such as potash alum (Ostwald). Members of the former class yield, even in dilute solution, a complex ion, which differs from the ions of either of the component salts, whereas true double salts yield the same ions as the single salts from which they have been formed. Thus the salt K_2PtCl_6 yields the complex anion $\overline{PtCl}_6$, whilst alum yields the same ions as potassium sulphate and aluminium sulphate. This distinction, however, is not absolute, since most double salts yield a certain proportion of complex ions, at all events in concentrated solution.

Complex salts are best regarded as the salts of complex acids or bases, and their chemical behaviour, as has already been pointed out (Vol. I., 125), is often quite different from that of their constituent salts.

Double salts. Although very many double salts have been prepared, very little is known as to the constitution of com-

pounds of this class. Their aqueous solutions as a rule exhibit the properties which would be expected of a mixture of the solutions of the component salts, although there is evidence in some cases of the existence in solution of an unstable complex. The relation of the solid salts to water is of great importance, and is discussed later (p. 118).

Among the double salts are found many series of isomorphous salts; a typical example is furnished by the double sulphates $R'_2SO_4,R''SO_4,6H_2O$, in which R′ represents the alkali metals K, Rb, and Cs, together with NH_4 and Tl′, whilst R″ represents the divalent metals such as Mg, Zn, Cd, Mn″, Fe″, Ni, and Co.

Solubility of Salts.

63 A very important property of salts is the manner in which they behave when treated with water. Strictly speaking, all salts are soluble to some extent in these circumstances, but in many cases the amount dissolved is so minute that for most purposes it may be neglected, and it is therefore usual to classify salts roughly as soluble, sparingly soluble, and insoluble, in water.

The extent of the variation in the solubility of different salts is illustrated by the following table, the figures in which represent the weight, in grams of anhydrous salt, dissolved by 100 grams of water at 15–18° C. The formula gives in each case the composition of the solid which is in equilibrium with the saturated solution at the same temperature.

Potassium carbonate, $K_2CO_3,2H_2O$.	110·5
Calcium chloride, $CaCl_2,6H_2O$ . . .	66
Sodium chloride, NaCl	35·9
Potassium nitrate, KNO_3	26
Potassium sulphate, K_2SO_4	10·3
Potassium perchlorate, $KClO_4$ . . .	1·5
Calcium sulphate, $CaSO_4,2H_2O$ . . .	0·20
Strontium sulphate, $SrSO_4$	0·011
Lead sulphate, $PbSO_4$	0·0041
Barium sulphate, $BaSO_4$	0·00026
Silver chloride, AgCl	0·00014
Silver bromide, AgBr	0·00001
Silver iodide, AgI	0·0000002

The solubility of a given salt has a definite value at each temperature. In a few instances, such as calcium hydroxide, and the calcium salts of certain organic acids, the solubility diminishes with rising temperature, but the great majority of salts exhibit an increase of solubility as the temperature rises. In some cases, such as that of potassium chloride, the solubility increases proportionally to the rise of temperature, *i.e.*, the solubility curve is a straight line, but, as a general rule, the curve becomes steeper as the temperature rises. Instances of this will be found in Fig. 8, where a number of solubility-temperature curves are reproduced, the abscissæ representing temperatures, and the ordinates the weights of salt dissolved by 100 grams of water.

The variation of solubility with temperature may be conveniently represented also by interpolation formulæ, the constants in which are deduced from direct experiment. Thus, if S represents solubility at the temperature $t°$ C., we have for potassium nitrate:

$$S = 13{\cdot}32 + 0{\cdot}5738t + 0{\cdot}01717t^2 + 0{\cdot}0000035 98t^3.$$

The process of dissolution of a salt in water is generally accompanied by absorption of heat, but there are many cases in which heat is evolved. The heat of solution, for instance, of a hydrated salt is generally negative, whereas that of the corresponding anhydrous salt is positive. Salts which do not form hydrates have, as a rule, a negative heat of solution.

The first action of water on a salt, or, speaking generally, of a solvent on any crystalline substance, is to liberate those molecules with which it is in contact, and to allow them to distribute themselves equally throughout the liquid; this process continues, provided an excess of the salt is present, until no more of the latter is dissolved, a condition of equilibrium being thus established between the solution and the salt. The condition of equilibrium is expressed by the solubility, which, as already shown, varies according to the nature of the salt and the temperature. Hence the solubility at a given temperature depends upon the exact nature of the solid present, and when a salt crystallises in two different forms the solubility may be different in the two cases. Thus it is that the solubility of an anhydrous salt is different from that of each of its hydrates, as, for example, in the case of calcium sulphate, which is much more soluble as

the hemihydrate than when combined with two molecules of water to form gypsum. This fact is of great practical importance, inasmuch as it is the cause of the setting of plaster of Paris (*q.v.*).

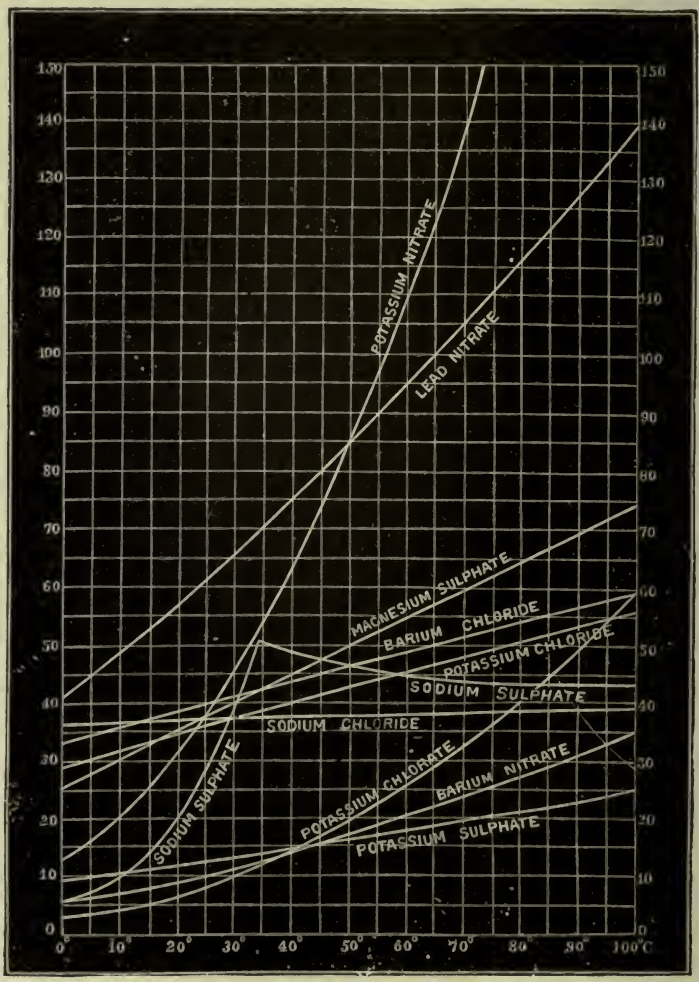


Fig. 8.

The fact that the solubility depends on the exact nature of the solid in equilibrium with the saturated solution has also supplied the explanation of certain cases of abnormal solubility, of which sodium sulphate is a typical example. As will be seen from the diagram, Fig. 8, the solubility of this salt rises

rapidly from 0° to 32·5°, but decreases from that point onwards, and is considerably less at 100°. It was formerly supposed that up to 32·5° the liquid contained the hydrate $Na_2SO_4,10H_2O$ in solution, and that above this temperature the latter underwent dissociation, the solution then containing the anhydrous salt. There is, however, no evidence of any sudden change in the properties of the solution, such as its vapour pressure or viscosity, at any point, and it has been shown that the above behaviour is really due, not to any change in the constitution of the liquid, but to a change in the solid substance with which the saturated solution is in equilibrium. Up to 32·5° the solid salt present is $Na_2SO_4,10H_2O$, and below that temperature the curve represents the solubility of this hydrate in water; at 32·5° the crystals of the hydrate are dissociated into water and anhydrous salt, and above that temperature the curve represents the diminishing solubility of the latter with rise of temperature; the curve, therefore, is a combination of two separate solubility curves which meet at 32·5°. When a solution which has been saturated at 32·5° is warmed, the anhydrous salt is deposited, whilst when it is cooled the hydrate $Na_2SO_4,10H_2O$ separates out.

64 The temperature 32·5°, at which the change from $Na_2SO_4,10H_2O$ to Na_2SO_4 occurs, is called the *transition temperature* for this pair of substances, and, like the melting point of a solid, is a perfectly definite temperature, depending only on the pressure. Above 32·5°, the decahydrate is unstable, below it, the anhydrous salt and water form an unstable system and unite to form the decahydrate. Such transition temperatures are very definite points, and on this ground may be employed in the standardisation of thermometers.[1] Like the melting point, moreover, the transition temperature is a point at which absorption of heat, change of volume, and change of vapour pressure occur, and it can be determined experimentally by observations of any of these effects.

The break in the solubility curve occurring at a transition temperature is generally much less marked than in the case of sodium sulphate. When each of the hydrates which are in equilibrium at the transition temperature becomes more soluble with rising temperature, the slopes of the solubility curves for the two compounds may not be very different. Instances

[1] See Richards and others, *Zeit. physikal. Chem.*, 1898, **26**, 690; **28**, 313; 1903, **43**, 465; 1906, **56**, 348; 1907, **61**, 313.

of this are found in connection with the hydrates of copper nitrate and lithium nitrate.

65 The examination of the relations of a salt to water in the manner exemplified above by the case of sodium sulphate is of great importance for the study of the various hydrates formed by the salt. In the investigation of the conditions of equilibrium in various systems of solids, liquids, and gases, of which the foregoing is a special case, each of the chemical substances present is called a *component* of the system, and each uniform solid, liquid, or gas present is termed a *phase*. The state of equilibrium of any such system is fully defined when the three variable factors of temperature, pressure, and concentration are known. These are not, however, always independent of each other, since in many systems when one of them is fixed the other two must also have fixed and invariable values. When hydrated sodium sulphate is in equilibrium with water, for example, only one of these factors can be independently varied, since a change in one of them brings with it a corresponding change in the others, and a new condition of equilibrium. Thus a change of temperature necessitates a change in the concentration and vapour pressure of the saturated solution. Such a system, in which it is necessary to fix only one of the three variable factors in order to have a fully defined state of equilibrium, is said to have one degree of freedom, and other systems exist which have two, three, or no degrees of freedom.

It has been found that the number of degrees of freedom depends entirely on the number of components and phases which are present, and the general law expressing the relation between these was established by Willard Gibbs in 1874, and is known as the *phase rule*. This states that, in any system which is in equilibrium, the number of degrees of freedom may be calculated by adding two to the number of components and subtracting the number of phases. Considering the case of the solubility of sodium sulphate in water, the components of the system are sodium sulphate and water. Below 32·5°, there are three phases, solid hydrated sodium sulphate, $Na_2SO_4,10H_2O$, liquid solution, and water vapour, and this system, as already mentioned, has one degree of freedom. At the transition temperature, when the solid decahydrate and the anhydrous salt co-exist in contact with the saturated solution, there are four phases, viz., the two solid phases just mentioned, together with the liquid solution and the water vapour. At this tempera-

ture, therefore, the system has no degree of freedom, and any change in one of the variable factors, for example, the temperature, will lead to the disappearance of one of the phases. Above 32·5°, there are again only three phases present, viz., solid anhydrous sodium sulphate, its saturated solution, and water vapour, and the system has as before one degree of freedom. The application of the phase rule to the study of equilibria cannot be further pursued here, and reference must be made to works on physical chemistry in which it is fully treated.[1]

66 The change of the decahydrate into the anhydrous salt does not invariably occur as soon as the transition temperature is passed, but may be delayed until a somewhat higher temperature is attained, provided that the anhydrous salt is absent; but if some of this is then introduced, the change commences at once, and proceeds until the whole of the decahydrate has been converted into the anhydrous salt. In a case like this the system is said to be *metastable, i.e.*, the system is in itself stable and no spontaneous change occurs, but as soon as a particular new phase is introduced the system at once becomes unstable and undergoes change with the production of this new phase. When, on the other hand, a system undergoes spontaneous change it is said to be *labile* or *unstable*.[2] A system can often exist in metastable equilibrium through a considerable range of temperature, and in fact some hydrates have been prepared which are known only in the metastable condition.

Sodium sulphate affords instances of all these phenomena. The solubility curve of the anhydrous salt (Fig. 9, curve *B*) has been traced below the transition point to 18°, and that of the decahydrate (curve *A*) above it to 34°. The dotted portions of the curves represent the solubility at temperatures beyond the transition point, in regions in which the systems are therefore in metastable equilibrium. These dotted curves are continuous with the curves obtained for the stable systems, and this circumstance shows clearly that the abnormality of the solubility curve of sodium sulphate is due to the fact that it is made up of portions of the two curves *A* and *B*, representing the solubilities of the two distinct substances $Na_2SO_4,10H_2O$ and Na_2SO_4. A third hydrate, $Na_2SO_4,7H_2O$, has also been

[1] Bancroft, *The Phase Rule* (Leipzig and Ithaca, 1897); Findlay, *The Phase Rule* (Longmans, 1904); Roozeboom, *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre* (Vieweg, Braunschweig, 1901).

[2] Ostwald, *Zeit. physikal. Chem.*, 1897, 22, 302.

prepared by allowing a solution of sodium sulphate to crystallise at 17°, and its solubility is shown by the curve *C*, which cuts the curve *B* at 24·2°. This substance is more soluble than the decahydrate throughout the whole course of the curve, and hence if a crystal of the decahydrate were introduced at any temperature into a solution saturated with the heptahydrate, $Na_2SO_4,10H_2O$ would crystallise out until the solution had the composition represented by the point on the curve *A* corresponding with the temperature at which the addition had been made. In other words, the heptahydrate is metastable throughout with respect to the decahydrate. This case is a typical one, for it is the rule that the solubility

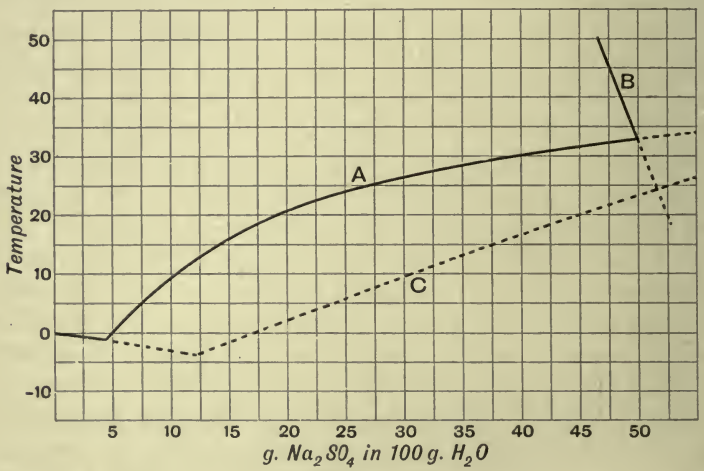


FIG. 9.

of a metastable hydrate is greater than that of the hydrate which is stable at the same temperature.

67 Somewhat different conditions prevail when the hydrated salt melts completely at a definite temperature, forming a single liquid phase of the same composition as the hydrate. In this case the hydrate behaves like an individual compound, and its melting point is accordingly lowered by the addition of any other soluble substance. It follows from this that the addition of either water or the anhydrous salt lowers the temperature at which the solid hydrate separates out, so that the melting point of the hydrate represents a point of maximum solubility. This is well shown in the case of ferric chloride,[1] Fe_2Cl_6, which forms

[1] Roozeboom, *Zeit. physikal. Chem.* 1892, **10**, 477. The formula Fe_2Cl_6 is chosen to obtain simple formulæ for the hydrates.

hydrates with 12, 7, 5, and 4 molecules of water, each of which exhibits this behaviour. The complete equilibrium curve for the hydrate with $12H_2O$ and its saturated solution is shown in Fig. 10, in which the solubility is expressed in molecules of Fe_2Cl_6 per hundred molecules of water. Curve *A*, extending from 0° to −55°, represents the temperatures of separation of ice from solutions of increasing concentration; the lowest temperature at which the hydrate with $12H_2O$ is formed is −55°, and the solubility rapidly rises (curve *B*) until 37° is reached, at which temperature

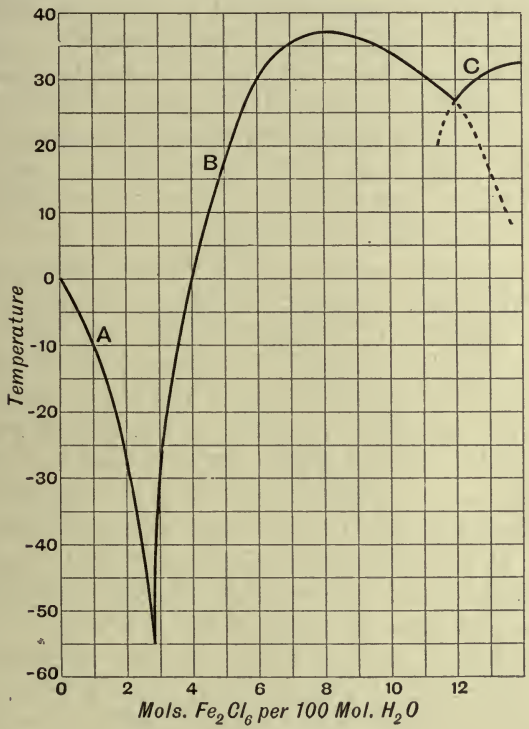


FIG. 10.

the hydrate melts. From this point, the temperature of equilibrium between the hydrate and the solution falls with increase of concentration, and this reflexed portion of the curve has been traced back as far as 8°. Below 27·4°, the equilibrium becomes metastable, since at this point the curve intersects the solubility curve (*C*) of the hydrate $Fe_2Cl_6,7H_2O$. Similar behaviour is shown also by the other hydrates of ferric chloride, by the hexahydrate of calcium chloride, and by many other analogous substances.

It is instructive to compare the solubility-temperature curves for salts which form well-defined hydrates with the freezing-point curves of binary alloys (see p. 79). The results obtained in both cases are to be interpreted in a similar manner.

68 *Double Salts.*—The conditions of formation and stability of double salts, and their behaviour towards solvents, form a subject of great importance, the development of which is due mainly to van't Hoff and Roozeboom. Only their main conclusions can be mentioned here. The formation of a double salt from two salts dissolved in water depends in the first place on the temperature of the system. In some cases the double salt can exist only below a certain temperature ($2KCl,CuCl_2,2H_2O$), in others it is formed only above a certain temperature ($Na_2SO_4,MgSO_4,4H_2O$), but in each case there is a transition temperature at which the double salt and its component single salts can exist together in the solid state in equilibrium with a saturated solution.

When equivalent amounts of hydrated sodium sulphate, $Na_2SO_4,10H_2O$, and hydrated magnesium sulphate, $MgSO_4,7H_2O$, are treated with a small quantity of water at 15°, a solution is obtained which is saturated with both substances and is in equilibrium with the solid salts. At 22°, which is the transition point for a mixture of these salts and astracanite, $Na_2SO_4,MgSO_4,4H_2O$, a certain amount of this double salt is formed, and there is then equilibrium between tho double salt, the two single salts, and the saturated solution. As the temperature rises above 22°, the single salts gradually dissolve and the less soluble astracanite separates out, and if the molecular solubility of the two single salts were equal, the whole of the solid would thus be converted at once into the double salt. Owing, however, to the greater solubility of magnesium sulphate, some sodium sulphate is at first left undissolved, whilst the solution contains more molecules of magnesium sulphate than of sodium sulphate. Thus at 23°, the solution contains about 1·4 mols. of magnesium sulphate to each molecule of sodium sulphate, whilst the solid present is a mixture of sodium sulphate with astracanite. This inequality finally disappears at 25°, and at this temperature solid astracanite alone is left in contact with a saturated solution containing the sulphates of sodium and magnesium in the same proportion as the solid salt. The range of temperature between 22° and 25° is termed the *transition interval,* and it is only at temperatures

beyond the transition interval that a double salt is not decomposed by water. Below 22°, then, astracanite, when brought into contact with water, is completely decomposed into its constituent single salts; at 22°, it exists in equilibrium with both of them; from 22° to 25°, it is decomposed with separation of sodium sulphate, and above 25° it is not decomposed by water at all.

Potassium cupric chloride, $2KCl,CuCl_2,2H_2O$, in contrast with astracanite, is stable in contact with its saturated solution at ordinary temperatures, but decomposes at 92°, the transition point, into potassium chloride and a new double salt, $KCl, CuCl_2$. Carnallite, $KCl,MgCl_2,6H_2O$, is completely decomposed by water at 167·8° into the chlorides of magnesium and potassium, and is partially decomposed at all temperatures below this with separation of potassium chloride, so that a pure saturated solution of carnallite in water cannot be prepared. Potash alum, on the other hand, is stable in presence of its solution at all temperatures up to 92·5°.

When the salts present are capable of undergoing chemical change, such as double decomposition, and when more than two single salts are present, the conditions of equilibrium become much more involved. Many extremely complicated cases have been examined by van't Hoff in a series of researches on the formation of the Stassfurt minerals, for an account of which the original papers must be consulted.[1]

69 Metallic salts are, as a rule, insoluble or very sparingly soluble in organic liquids. Some liquids, however, such as alcohol, acetic acid, ether, acetone, pyridine, benzonitrile, &c., dissolve certain salts with some freedom. Thus calcium chloride, calcium nitrate, potassium iodide, and many others are soluble in alcohol, whilst mercuric chloride and zinc chloride are soluble both in alcohol and ether, and the solubility of cadmium bromide in a mixture of these two solvents has been made use of in the wet processes of photography. Salts which are insoluble in alcohol are precipitated in the form of minute crystals when alcohol is added to their aqueous solutions, and this substance is therefore often used in quantitative analysis, having been first proposed for this purpose by Bergman in 1778.

[1] van't Hoff, *Bildung und Spaltung von Doppelsalzen. Zur Bildung der ozeanischen Salzablagerungen* (Braunschweig, 1905). See also E. F. Armstrong, *British Assoc. Reports*, 1901, 262; Findlay, *The Phase Rule*, p. 283.

70 *Supersaturated Solutions.*—When a solution of a salt free from any undissolved crystals is allowed to cool quietly in closed vessels, it is frequently observed that no crystals separate out, although the quantity of salt contained in the liquid is greater than that which can exist in solution at that temperature in contact with the solid salt. Such solutions are termed *supersaturated.* If, however, a crystal of the salt is added, a rapid crystallisation occurs, and the clear solution is then found to contain the normal amount of dissolved salt. Sodium acetate shows the phenomenon of supersaturation in a striking manner. For this purpose the crystallised salt is gently warmed in a flask with one quarter of its weight of water until all is dissolved; the liquid, if not perfectly free from suspended matter, is then filtered into a flask, the neck of which is then closed with a plug of cotton-wool. If the smallest crystal of sodium acetate is thrown into the liquid when cold, crystallisation at once commences round the small particle, and in a few seconds the whole has assumed the solid form, the change being accompanied by a considerable rise of temperature.

When a hot saturated solution of a salt is allowed to cool in the absence of the solid salt, the supersaturated solution which is produced is at first metastable (p. 115), and during this period crystallisation can be brought about only by the introduction of a crystal of the solid salt, or of one isomorphous with it. As soon as a certain temperature is reached, however, the solution becomes unstable or labile, and crystallisation then occurs spontaneously, its first appearance being much aided by stirring and friction. At each temperature, therefore, the solution remains metastable only up to a certain definite limit of concentration, beyond which it becomes labile.[1] A curve of "supersolubility" can thus be constructed for each salt, and it is found that such a curve is, as a rule, approximately parallel to the solubility curve. The exact temperature at which the change from the metastable to the labile state occurs is best determined by observing the sudden change in the refractive index of the well-stirred solution which accompanies the separation of crystals. Thus a solution of sodium nitrate containing 48·8 per cent. of the salt becomes labile at 20°; spontaneous crystallisation then occurs, and the concentration of the solution falls to that of a saturated solution at this temperature, which contains 45·8 per cent. of the salt. A solution of the

[1] Miers and Isaac, *Journ. Chem. Soc.*, 1906, **89**, 413.

same salt containing 51·2 per cent. of salt becomes labile at 30°.

The indifference of a supersaturated solution to crystals of non-isomorphous salts can readily be shown experimentally. A supersaturated solution of sodium acetate, prepared as described above, is poured gently on to the surface of a supersaturated solution of sodium thiosulphate, made by simply melting the crystals of the hydrated salt in a long test-tube. If, after cooling, a crystal of sodium thiosulphate is dropped into the tube, it falls through the lighter solution of sodium acetate without inducing crystallisation, but causes the immediate formation of crystals as soon as it comes into the heavier solution of sodium thiosulphate. A supersaturated solution of magnesium sulphate may be made to crystallise by adding either magnesium sulphate itself, or any one of the isomorphous sulphates of iron, zinc, nickel, &c., whilst sodium sulphate, sodium chloride, &c., have no action upon it. Supersaturated solutions of sodium sulphate crystallise very readily when exposed to the air, and it has been shown that this is due to the presence of minute crystals of this salt in the atmosphere.

The amount of a solid salt required to induce crystallisation in a metastable solution is extremely small, amounting to about one ten-millionth of a milligram (10^{-10} gram) in the case of sodium chlorate.[1] Whether this minimum amount varies with the degree of supersaturation of the solution has not yet been ascertained.

Fusibility and Volatility of Salts.

71 Most of the metallic salts melt at temperatures beyond the range of the ordinary mercurial thermometer, but many melting points have been determined with accuracy by means of resistance or thermo-electric pyrometers. As already mentioned (p. 64), Carnelley has shown that, in the case of the salts which the metals form with the same acid, the melting point is a periodic function of the atomic weight of the metal contained in the salt, just as is the case with the metals themselves.

The boiling point has been determined only in the case of a few halides, but the comparative volatility of certain salts was approximately ascertained by Bunsen[2] by the

[1] Ostwald, *Zeit. physikal. Chem.*, 1897, **22**, 289.

[2] *Phil. Mag.*, 1866 (4), **32**, 85.

following method. A small bead of each salt weighing one centigram is placed in the zone of fusion of a Bunsen flame having a temperature of about 1300°, and the time ascertained which the bead takes to volatilise. The following numbers give the relative volatility for certain salts, that of sodium chloride being taken as the standard:

	NaCl	KCl	KBr	KI	K_2SO_4	K_2CO_3
Seconds.	84·2	63·4	41·0	29·8	665·2	272·0
Volatility.	1·000	1·288	2·055	2·828	0·127	0·310

It has been shown by Bailey[1] that certain salts are slightly volatile when their aqueous solutions are evaporated, even when all precautions are taken to prevent their being carried over mechanically. This phenomenon has been more closely examined in the case of the chlorides of the alkali metals, and it has been shown that the volatility increases with the molecular weight of the chloride and the concentration of the solution.

Generic Properties of Salts.

72 The generic properties of the metallic salts have in most cases been already given in Vol. I., under the respective acids. The most important points, however, are shortly recapitulated here.

Fluorides.—In their general properties the fluorides closely resemble the chlorides, but are, as a rule, much less soluble in water. Potassium, ammonium, silver, and stannous fluoride dissolve readily, the sodium and lithium salts less easily, those of the alkaline earth metals very sparingly, whilst the remainder are almost insoluble. The alkali fluorides unite with hydrogen fluoride, and with the fluorides of the more electronegative elements, to form double fluorides, which usually crystallise well. Thus we have:

Potassium hydrofluoride, KF,HF = KHF_2
Potassium borofluoride, KF,BF_3 = KBF_4
Potassium silicofluoride, 2KF,SiF_4 = K_2SiF_6
Potassium tantalofluoride, 2KF,TaF_5 = K_2TaF_7.

Chlorides.—The greater number of the chlorides are solids, but a few, such as stannic chloride, $SnCl_4$, titanic chloride, $TiCl_4$, and antimony pentachloride, $SbCl_5$, are liquids, and

[1] *Journ. Chem. Soc.*, 1894, **65**, 445.

these, as well as mercuric chloride, $HgCl_2$, and antimony trichloride, $SbCl_3$, may be readily volatilised. The majority melt at a fairly high temperature, and can be volatilised only at a red heat or higher temperature. A few, such as gold chloride, $AuCl_3$, and platinum chloride, $PtCl_4$, decompose into their elements when strongly heated. With the following exceptions, they dissolve readily in water: aurous chloride, AuCl, silver chloride, AgCl, mercurous chloride, Hg_2Cl_2, cuprous chloride, Cu_2Cl_2, platinous chloride, $PtCl_2$, palladious chloride, $PdCl_2$, thallous chloride, TlCl, and lead chloride, $PbCl_2$; the last two dissolve to a slight extent in cold, and readily in hot water.

In some cases the chlorides are chemically acted on by water, giving rise to basic compounds; thus, the trichlorides of bismuth and antimony yield insoluble oxychlorides:

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

Others, such as titanium chloride, are completely decomposed into hydrochloric acid and a hydroxide of the metal.

Many double chlorides are also known, similar to the double fluorides, but the tendency to the formation of the former is not so strong. The most characteristic are the *platinichlorides*, such as potassium and ammonium platinichlorides, K_2PtCl_6 and $(NH_4)_2PtCl_6$, which may be regarded as salts of the acid H_2PtCl_6.

Bromides and *Iodides* closely resemble the corresponding chlorides.

Cyanides.—These salts are classed with the halides, which they closely resemble in properties. The cyanides of the alkali and alkaline earth metals and mercury are soluble in water; the remainder are insoluble, but dissolve in a solution of potassium cyanide, forming double cyanides.

Some of these double cyanides are properly described as complex salts, no longer giving the reactions of the characteristic metal (other than potassium) which is present. Thus, potassium ferrocyanide and ferricyanide in neutral or acid solution do not give the reactions which are typical of ordinary ferrous and ferric salts. According to the electrolytic dissociation theory, the iron in the ferro- and ferri-cyanides is part of a complex negative ion, the reactions of which are quite different from those of the positive iron ion.

The complex formation is less stable in the case of potassium silver cyanide, $KAg(CN)_2$, obtained by the action of potassium

cyanide on silver cyanide. In aqueous solution this substance appears to be dissociated mainly into the ions $\overset{+}{K}$ and $Ag(\overline{CN})_2$, for when the solution is electrolysed the silver migrates towards the anode as part of the negative ion. A solution of potassium silver cyanide gives only a few of the ordinary reactions of silver salts: that it does so at all is probably due to the presence of a small quantity of $\overset{+}{Ag}$ ion, arising from the slight dissociation of the $Ag(CN)_2$ ion.

Differences in the stability of double cyanides are utilised in the qualitative separation of copper and cadmium on the one hand, and of nickel and cobalt on the other.

Hypochlorites.—The salts of hypochlorous acid are almost unknown in the free state, as they are generally obtained together with chlorides by the action of chlorine on cold solutions of the hydroxides of the metals, and cannot be isolated from the solution.

Chlorates.—The chlorates are all soluble in water, that of potassium being one of the least soluble, and they all decompose on heating, giving off oxygen and leaving the chloride.

Perchlorates.—These salts are also, without exception, soluble in water, the least soluble being the potassium salt; like the salts of the other oxy-acids of chlorine, they are completely decomposed by heat into oxygen and the chloride of the metal.

Iodates and Periodates.—Several series of both iodates and periodates are known, which have already been described (Vol. I., pp. 369, 371).

Sulphides.—The compounds of the metals with sulphur correspond in general with the oxides, although there are cases in which no sulphide is known corresponding to a particular oxide, and *vice versa.* The sulphides and hydrosulphides of the alkali metals and the hydrosulphides of metals of the alkaline earths are soluble in water; the solutions when allowed to remain in contact with free sulphur are converted into polysulphides, and are oxidised by the oxygen of the air to sulphites, thiosulphates, and sulphates. The remaining sulphides are almost all insoluble in water, some of them being dissolved by dilute acids with evolution of sulphuretted hydrogen, whilst others undergo no change under these conditions. The different solubilities of the sulphides in water and acids are utilised in the qualitative and quantitative separation of the metals.

The sulphides of the more electro-negative metals dissolve in solutions of the alkaline sulphides, forming sulpho-salts, just as the corresponding oxides unite together to form oxy-salts. Thus potassium oxide combines with arsenic oxide to form potassium arsenate, and potassium sulphide combines with arsenic sulphide to form potassium thioarsenate:

$$3K_2O + As_2O_5 = 2K_3AsO_4$$
$$3K_2S + As_2S_5 = 2K_3AsS_4.$$

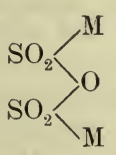
Subjoined is a list of some of the analogous oxy-salts and sulpho-salts which have been prepared, in the formulæ of which M represents an atom of a monad metal.

Oxy-salts	Sulpho-salts
Carbonates, M_2CO_3	Thiocarbonates, M_2CS_3
Pyrophosphates, $M_4P_2O_7$	Pyrothiophosphates, $M_4P_2S_7$
Metarsenates, $MAsO_3$,	Metathioarsenates, $MAsS_3$
Orthoarsenates, M_3AsO_4	Orthothioarsenates, M_3AsS_4
Metastannates, M_2SnO_3	Metathiostannates, M_2SnS_3
Orthostannates, M_4SnO_4	Orthothiostannates, M_4SnS_4.

Similar salts are also known containing selenium and tellurium in place of sulphur.

Sulphites.—Sulphurous acid, being a dibasic acid, forms two series of salts, viz., normal and acid sulphites, such as Na_2SO_3 and $NaHSO_3$. Those of the alkali metals are soluble in water, but the remainder are for the most part sparingly soluble or insoluble, although they dissolve in a solution of sulphurous acid. They are fairly stable in the dry state, but gradually oxidise in presence of moisture, forming sulphates.

In addition to these, a series of sulphites known as the *metabisulphites* or *disulphites* has been prepared, the constitution of which is probably represented by the general formula:



Sulphates.—With the exception of those of barium, strontium, and lead, which are almost insoluble in water, and those of calcium, silver, and mercury, which are sparingly soluble, all the sulphates dissolve readily; on evaporation, the solutions

yield well-developed crystals, usually containing water of crystallisation. The metals of the alkalis form normal and acid sulphates, the metals of the alkaline earths and magnesium yield only normal sulphates, whilst many other metals form soluble normal salts, as well as more or less insoluble basic sulphates. Many sulphates possess the property of forming crystallisable double salts. This is especially the case with the sulphates of the isomorphous metals of the magnesium group, which yield compounds with the sulphates of the alkali metals having the general formula $M^{ii}SO_4,M^{i}_2SO_4,6H_2O$, for instance, schönite, $MgSO_4,K_2SO_4,6H_2O$.

Another important group of the double sulphates is that of the *alums*, which have the general formula $M^{iii}_2(SO_4)_3,M^{i}_2SO_4,24H_2O$; for example:—

$Al_2(SO_4)_3,K_2SO_4,24H_2O$, $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$,
$Cr_2(SO_4)_3,K_2SO_4,24H_2O$, $Al_2(SO_4)_3,Na_2SO_4,24H_2O$,
$Al_2(SO_4)_3,Ag_2SO_4,24H_2O$, $In_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$.

Nitrides. Many of the metals such as magnesium, calcium, vanadium, titanium, and lithium, unite with nitrogen when strongly heated in the gas, forming stable nitrides, but in other cases these compounds can be obtained only indirectly by the action of ammonia on the heated oxides or chlorides. They are usually dull brown or black powders, the composition of which has in many cases not been accurately determined, and a number of them are undoubtedly mixtures.

The salts of azoimide (Vol. I., p. 517) form a special class of nitrides which contain the group $.N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$; these are all extremely explosive substances.

Nitrites.—These salts are for the most part soluble in water, and are decomposed when strongly heated into oxides of nitrogen and the oxide of the metal. Dilute mineral acids decompose nitrites, yielding nitric oxide.

Nitrates.—With the exception of one or two basic nitrates, such as that of bismuth, all the nitrates dissolve in water, and usually crystallise well. They melt at low temperatures, and on further heating those of the alkali and alkaline earth metals are converted, first into nitrites with evolution of oxygen, and then into oxides of nitrogen and the oxide of the metal; with the nitrates of the other metals the intermediate formation

of nitrite is not usually observed, and in cases where the oxide is unstable at high temperatures the metal itself remains as the final product. Owing to the ease with which they lose oxygen, the nitrates are frequently employed as oxidising agents.

Phosphides.—Most of the metals combine with phosphorus to form phosphides. Some of these, for example, the phosphides of iron and zinc, are crystalline, but a large number have been obtained only as difficultly fusible masses, which have not as yet been closely examined, and are probably far from pure. Those of the alkali and alkaline earth metals are decomposed by water with formation of gaseous or liquid hydrogen phosphide.

Hypophosphites, Phosphites, Phosphates, Arsenites, and Arsenates.—The relations between the different modifications of the corresponding acids, and the general properties of their salts, have already been fully described (Vol. I., pp. 645–668, 692–700).

Carbides.—Most of the metals combine with carbon when either they or the oxides are heated together with carbon to a very high temperature in an electric furnace. Those of the alkali and alkaline earth metals are decomposed by water with formation of the hydroxide and evolution of acetylene, whilst that of aluminium yields methane in place of acetylene. Many of the other carbides crystallise well, and of these by far the most important are those of iron; they are always present in commercial iron and exert an immense influence on its properties.

Carbonates.—Most of the metals form salts with carbonic acid, the monovalent alkali metals yielding normal and acid salts of the general formulæ M_2CO_3 and $MHCO_3$; a few metals, such as aluminium and chromium, do not appear to form carbonates; and others, such as magnesium, bismuth, and copper, yield basic carbonates.

With the exception of the carbonates of the alkali metals and of thallium, all the carbonates are insoluble in water, but many of them dissolve in water containing carbonic acid, probably owing to the formation of an unstable acid carbonate. They are decomposed by heat with evolution of carbon dioxide and formation of the oxide of the metal, unless this is itself decomposed at the temperature employed. The temperature at which the decomposition takes place varies considerably:

thus, the carbonates of the alkali metals are only slightly decomposed at a bright red heat, whilst those of the alkaline earth metals are completely decomposed at this temperature, if the carbon dioxide is removed as it is formed; the other carbonates decompose for the most part at a lower temperature.

Borates and Silicates.—These salts have already been discussed (Vol. I., pp. 728–730; 917–920).

CHEMICAL CHANGE AND THE LAW OF MASS ACTION.

73 *Reversible or Balanced Reactions.*—The older chemists thought that substances combined with one another only when they possessed a common principle, and hence they gave the name of "affinity" (*affinis*, related) to the particular property in virtue of which substances unite. It was afterwards seen that substances which have nothing in common nevertheless react with one another chemically, and this was ascribed to a mutual attraction between the particles of the substances (Newton). It was thought, moreover, that this attraction was elective in its character, so that when the particles of three substances were all brought together, those two would combine between which there was the strongest attraction, to the exclusion of the third. Thus, if a substance A, capable of uniting with C, were presented to a compound BC, made up of two substances united together, no change would occur if the attraction of C for B were stronger than that of C for A; whilst, if the opposite were the case, C would unite with A, and leave B in the free state. This view was supported especially by Geoffroy (1718) and Bergman (1775), who drew up tables of affinity or attraction, showing the order of strength of the affinities of the various bases, metals, &c., for the acids and other substances with which they were capable of combining. The true state of affairs was, however, first recognised by Berthollet, who demonstrated by a series of experiments that the course of a reaction does not depend solely on the affinities of the substances concerned, but also on the relative quantities of them which are present. Thus, according to the view held by Berthollet, it follows that "in opposing the body A to the combination BC, the combination AC can never take place; but that the body C will be divided between the bodies A and B proportionally to the affinity and the quantity

of each."[1] These views were afterwards developed by Berthollet in his celebrated *Essai de Statique Chimique.*

The further progress of investigation in this department of chemistry[2] has confirmed the opinions expressed by Berthollet. When careful experiments are made it is frequently found that a reaction does not proceed until one or other of the substances concerned has entirely disappeared, but that a certain fraction of the original substances remains unaltered. In those cases where a complete reaction appears to occur, equilibrium is reached only when an exceedingly small proportion of the substances originally concerned is left unchanged.

Thus, when calcium carbonate is heated in a closed vessel it evolves carbon dioxide until a certain pressure of this gas is reached, after which no further change in composition occurs until the conditions are in some way altered. If the temperature is raised, more carbon dioxide is evolved, until another definite pressure, higher than the previous one, is attained, after which the system again undergoes no further change so long as the circumstances remain unaltered. It is, moreover, found that to every temperature there is a corresponding equilibrium pressure of carbon dioxide, which is perfectly definite and constant. The increase of the equilibrium pressure with rising temperature is shown by the following figures[3]:—

Temperature.	Pressure.
547°	27 mm. of mercury.
610	46 „ „
740	255 „ „
810	678 „ „
865	1333 „ „

If, on the other hand, the temperature is kept constant, but the pressure of the carbon dioxide is lowered by pumping out some of the gas, an additional quantity of the calcium carbonate decomposes until the original pressure is again attained. In order to decompose calcium carbonate completely by heat it is therefore necessary to keep the pressure of the carbon dioxide

[1] *Researches into the Laws of Chemical Affinity*, p. 6 (English Translation, London, 1804).

[2] A fuller account of this subject will be found in Lothar Meyer, *Modern Theories of Chemistry;* Nernst, *Theoretical Chemistry;* Ostwald, *Allgemeine Chemie*, vol. ii.; Mellor, *Chemical Statics and Dynamics* (Longmans, 1904).

[3] Le Chatelier, *Compt. rend.*, 1886, **102**, 1243.

as low as possible. This is effected by heating the carbonate in a current of air freed from carbon dioxide, or, more usually, in the open air ; in this latter case the pressure of carbon dioxide is negligibly small, and hence in the ordinary form of the experiment, *e.g.*, the "burning" of limestone, the decomposition is practically complete. The reactions on which Brin's process for the manufacture of oxygen (Vol. I., p. 246) is based, furnish another illustration of the extent to which the decomposition of a compound may be influenced by the pressure of one of the products of decomposition.

Many reactions, then, are not complete, but proceed only until a certain definite state of equilibrium is set up. This state of equilibrium is quite analogous to what occurs in many physical phenomena. Thus, when water or any liquid evaporates in a confined space, the evaporation proceeds only until the vapour of the liquid exerts a certain definite pressure on the surface of the liquid ; this equilibrium pressure is constant for any particular temperature, and increases rapidly as the temperature rises. When the condition of equilibrium has been attained, the relative amounts of vapour and liquid are unaltered so long as the other conditions remain the same. The maintenance of this state of equilibrium depends upon the fact that the evaporation of the liquid is proceeding at exactly the same rate as the condensation of the vapour, so that the actual proportion of vapour to liquid remains the same, whilst individual particles of the liquid are continually escaping from its surface, and as many others returning to it from the vapour above.

Precisely the same considerations hold with regard to chemical equilibrium. Thus, recurring to the example of calcium carbonate, we may suppose that when equilibrium is set up at any particular temperature, the calcium carbonate is being decomposed into lime and carbon dioxide at exactly the same rate as these two compounds are combining to form calcium carbonate.

All simple chemical equilibria may be similarly regarded as resolvable into two reactions proceeding in opposite senses and at equal rates, so that the actual proportions of the substances present undergo no change. Chemical changes of this kind, which can proceed in either sense according to the circumstances of the experiment, and which finally reach a definite position of equilibrium, are known as reversible or balanced

reactions, and are often indicated symbolically by a special sign placed between the two parts of the equation:—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

As already suggested, it is probable that all chemical changes really belong to the class of reversible reactions, although in a great many cases the position of equilibrium lies very much at one extreme, and the reversibility cannot be realised in practice.

74 *Velocity of Reaction.*—We have conceived the equilibrium reached in a reversible reaction as a dynamic one, depending on the equal and opposite effects of two opposing reactions; it is therefore of great importance to ascertain what conditions determine the velocity of a reaction. The attainment of equilibrium takes time, although in many cases the reaction proceeds so rapidly that this time cannot be measured; thus, when hydrochloric acid is added to caustic soda solution, when silver nitrate is added to solution of sodium chloride, and in many similar instances, the reaction appears to be complete as soon as the substances have been brought into contact, and no measurement of the rate of the reaction is possible. When, however, the reaction proceeds slowly, such measurements can be made, and it is thus possible to ascertain the influence of various factors on the velocity of the change.

The most important result of the experiments which have been made on this subject is the generalisation known as the law of mass action, which states that the velocity of any reaction is directly proportional to the concentrations (or active masses) of the substances concerned. This law follows from the investigations of Wilhelmy (1850), Harcourt and Esson (1866), Guldberg and Waage (1867), van't Hoff, and others.

The law may be definitely formulated in the following way. Let us suppose that we are dealing with the reversible reaction $A + B \rightleftharpoons C + D$, and that the concentrations of the four substances involved are, at the moment, p, q, p', and q' respectively. If v is the velocity of the forward reaction, *i.e.*, the rate at which A and B unite to form C and D, then, according to the law of mass action, $v = kpq$, where k is the so-called velocity coefficient, and has a definite value for a given reaction at a constant temperature. Similarly, if v' is the velocity of the back reaction, *i.e.*, the rate at which C and D are uniting to form A and B, we have $v' = k'.p'q'$, k' also being a velocity coefficient. The velocity of the resultant reaction,

which alone can be measured by experiment, will then be $v - v' = kpq - k'p'q'$. If the reaction is one in which the position of equilibrium lies at the right hand extreme, *i.e.*, if the change proceeds until either A or B has practically disappeared, then the back reaction may be neglected, and the velocity of the reaction as a whole is given by the formula: $v = kpq$.

The experiments of Harcourt and Esson [1] may be cited as an instance of the results obtained in studying the applicability of the law of mass action. They were carried out by allowing potassium permanganate to act on oxalic acid dissolved in water in presence of manganese sulphate, which is necessary to the reaction, and sulphuric acid. The amounts of the various substances present could all be varied, and the reaction was very thoroughly investigated. The amount of unaltered potassium permanganate present in the solution at any moment was determined by adding an excess of potassium iodide solution and estimating the iodine liberated.

The simplest case of this reaction occurs when the oxalic acid is in large excess, as in these circumstances the change of concentration of this substance may be neglected. It is then found that under these conditions the rate at which the potassium permanganate is disappearing at any moment is proportional to the amount still left unreduced. This may be expressed more simply by saying that the same fraction of the permanganate still present in the solution is reduced in each successive equal interval of time. In the following table the experimental figures obtained with a mixture of the molecular composition $2KMnO_4 + 14MnSO_4 + 108C_2H_2O_4$ are compared with those calculated on the assumption that the law of mass action holds for this particular change; as will be seen, the agreement is excellent:

Time.	Amount of Permanganate left in the solution.	
	Observed.	Calculated.
2	94·8	94·8
5	87·9	87·6
11	74·9	74·7
27	49·3	48·9
35	39·1	39·6
47	28·3	28·8
68	17·0	16·5

[1] *Phil. Trans.*, 1866, **156**, 193.

In reactions in which the concentrations of two substances are both altering at the same time, such as the saponification of ethyl acetate by caustic soda,

$$C_2H_3O_2C_2H_5 + NaOH = C_2H_5OH + NaC_2H_3O_2,$$

the matter is more complicated, since the rate of the reaction at any moment is now proportional to the product of the active masses of the two substances at that moment. Here again, however, the observed numbers agree well with those obtained by calculation from the law of mass action. In many cases, especially when solutions of weak acids or bases are concerned, the active mass is not that of the total substance present, only that portion of the substance which is electrolytically dissociated taking an active part in the change. Thus, when an equivalent amount of ammonia, which is dissociated to a much smaller extent than caustic soda, is substituted for the latter in the above reaction, the rate of saponification becomes much slower, and is still further diminished by the addition of any substance, such as an ammonium salt, which lessens the dissociation of the ammonia.

Rise of temperature has a very marked effect on the rate of chemical change, and, on the average, the velocity of reaction is trebled for a rise of 10° C. The very high value of the temperature coefficient of reaction velocity makes it intelligible that substances which, at certain temperatures, react rapidly and reach a position of equilibrium, have yet no apparent action on each other at much lower temperatures. Thus, a mixture of hydrogen and oxygen, which cannot be in true equilibrium, can be kept for any length of time at the ordinary temperature without an appreciable quantity of water being produced.

The accurate investigation of reaction velocities has been of great service in the study of catalytic action. The value of the velocity coefficient obtained for a catalytically accelerated reaction is a measure of the efficiency of the catalytic agent. Thus, by comparing the values obtained for the velocity coefficient in different experiments, one can ascertain how the efficiency of a catalytic agent is affected by the conditions under which it works, and how the efficiency of one catalytic agent compares with that of another under the same conditions.[1]

[1] For a short account of the study of catalysis on these lines, see the article on "Chemical Affinity," in Thorpe's *Dictionary of Applied Chemistry* (1912).

75 *Chemical Equilibrium.*—The velocity with which a reversible reaction approaches its point of equilibrium is, as already shown (p. 132), given by the formula :—

$$v - v' = k.pq - k'.p'q'.$$

When equilibrium is reached, $v - v' = o$, and therefore, $k.pq = k'.p'q'$, or $\frac{k}{k'} = \frac{p'q'}{pq}$, where p, q, p', q', are now the concentrations of A, B, C, and D respectively at the point of equilibrium. The ratio $\frac{k}{k'} = \mathrm{K}$ is known as the *equilibrium constant*, and can be determined experimentally by ascertaining the amounts of the various substances which are actually present when equilibrium is established.

Thus, when alcohol is mixed with acetic acid, the following reaction occurs :

$$C_2H_5.OH + C_2H_4O_2 \rightleftharpoons C_2H_5O.C_2H_3O + H_2O.$$

If known quantities of acid and alcohol are taken, the amount of change which has occurred during any period can readily be measured by titrating the acid still present, and subtracting the amount thus found from that originally taken. The quantities of alcohol, ethyl acetate, and water present can then all be calculated from this number by means of the equation representing the reaction. If equivalent amounts of acid and alcohol are taken, it is found when equilibrium is established, a process which requires several days at the ordinary temperature, that $\frac{2}{3}$ of the alcohol and acetic acid have undergone the reaction, whilst $\frac{1}{3}$ of each is left unaltered. Exactly the same state of equilibrium is reached if equivalent amounts of ethyl acetate and water are allowed to react. In this condition, therefore, $pq = \frac{1}{3} \times \frac{1}{3} = \frac{1}{9}$, whilst $p'q' = \frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$, so that

$$\mathrm{K} = \frac{p'q'}{pq} = 4.$$

When the value of the equilibrium constant has once been determined, it is possible to calculate the composition of the equilibrium mixture when the reacting substances are taken in other than equivalent proportions. Thus, if a molecules of alcohol and b molecules of acetic acid are taken in the above

instance, and if x is the number of molecules of ester present in the equilibrium mixture, then

$$p = a-x,\ q = b-x,\ p' = q' = x.$$

By substituting these values in the equation given above, the value of x can be obtained. The numbers calculated in this way agree well with those obtained by experiment.

It is found experimentally, in harmony with the formula for the equilibrium constant, that if a large excess of alcohol is taken, practically the whole of the acetic acid is converted into ethyl acetate, whilst if a large excess of acid is taken almost the whole of the alcohol undergoes the reaction. These facts have an important bearing upon the reactions used in analytical processes. In these cases it is essential that equilibrium be not established until practically the whole of the substance which is being estimated has undergone the particular reaction. In the processes of gravimetric analysis the substance which is being analysed, or some one of its elements, is converted into a sparingly soluble compound. In this way the product which is precipitated is continually withdrawn from the solution, the equilibrium is thereby disturbed, and fresh quantities of the substance are formed and precipitated, the reaction thus proceeding until it is practically complete. This effect is further aided in most cases by the use of an excess of the reagent, which, as we have just seen, tends to increase the extent to which the other substance undergoes the reaction. In the processes of volumetric analysis it is also necessary to choose reactions for which the equilibrium constant is very high, and which, moreover, proceed rapidly. Thus, the reaction between equivalent quantities of caustic soda and hydrochloric acid can be utilised for estimating the amount of the former present, because the reaction proceeds rapidly, and equilibrium is established only when practically the whole of the acid and alkali present have reacted. The completion of the reaction is therefore indicated by the fact that the solution becomes neutral. On the other hand, it is impossible to estimate alcohol by titration with hydrochloric acid, because the constant of equilibrium for this reaction is low (8·44 at 99°[1]), and equilibrium is attained long before the whole of the alcohol has been converted into ethyl chloride, and therefore before the solution has become neutral, so that it is

[1] Cain, *Zeit. physikal. Chem.*, 1893, **12**, 751.

impossible to ascertain by the aid of an indicator when an equivalent of the acid has been added.

Many cases of chemical equilibrium have been experimentally studied on the lines indicated above. Special mention may be made of the investigation of the following reactions, some of which are of technical importance:—$CO_2 + H_2 \rightleftharpoons CO + H_2O$(1); $2SO_2 + O_2 \rightleftharpoons 2SO_3$(2); $4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$(3); $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$(4).

The study of gaseous dissociation from the point of view of the law of mass action presents many interesting features. When a gas is decomposed by heat into several new molecules, which may either be all of the same kind, as in the case of nitrogen peroxide, N_2O_4, or of different kinds, as in the case of phosphorus pentachloride, and these reunite to form the original gas when the whole is allowed to cool, the gas is said to dissociate when heated. In the case of such a partly dissociated vapour the quantities of the several gases present are proportional to their partial pressures in the mixture. Thus, if p be the pressure due to the undissociated molecules, and p_1 that of each of the two new gases formed, the equation of equilibrium becomes

$$K = \frac{p_1^2}{p}.$$

If now the pressure of one of the products of dissociation is increased by adding some of it to the mixture without altering the volume, it follows that the numerator of this fraction must increase, and that therefore, since K must remain constant, p must also increase. In other words, the dissociation of the gas must be diminished. This result has been experimentally verified in many cases. Thus when phosphorus pentachloride is vaporised, it dissociates partially into phosphorus trichloride and chlorine:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2.$$

When, however, the pressure of either the phosphorus trichloride vapour or the chlorine is increased, the dissociation of the gas is diminished, and the vapour density is increased. The

[1] Hahn, *Zeit. physikal. Chem.*, 1903, **44**, 513.

[2] Bodenstein and Pohl, *Zeit. Elektrochem.*, 1905, **11**, 373.

[3] von Falckenstein, *Zeit. physikal. Chem.*, 1907, **59**, 313; 1909, **65**, 371.

[4] Deville, *Compt. rend.*, 1870, **70**, 1105, 1201; **71**, 30; Preuner, *Zeit. physikal. Chem.*, 1904, **47**, 385.

same is true for ammonium chloride, which does not dissociate to so large an extent in presence of ammonia or hydrogen chloride.

A similar phenomenon occurs in solutions of electrolytes; when two substances having a common ion are present in a solution, neither of them is electrolytically dissociated to as great an extent as it would be were the other substance absent.

The effect of temperature and pressure on chemical equilibrium has also been carefully studied for many partially dissociated gases. The particular state of equilibrium attained by any system of reacting substances depends on the physical conditions to which the system is subjected, but the extent by which the state of equilibrium is altered by change of temperature and pressure varies very largely according to the nature of the special reaction concerned. It may be taken as a general law that rise of temperature tends to produce such a change in the equilibrium of the system as is attended by an absorption of heat, whilst a lowering of the temperature has an effect in the opposite direction. Thus, when a gas such as nitrogen peroxide, N_2O_4, is heated to a definite temperature it decomposes to a perfectly definite extent into molecules of the simpler gas, NO_2, a change which is accompanied by absorption of heat. If now the temperature is raised, the effect is to increase the dissociation of the gas in harmony with the general law just enunciated. If a reaction proceeds without much evolution or absorption of heat, the effect of change of temperature on the position of equilibrium is correspondingly small: an instance of this is furnished by the reaction between ethyl alcohol and acetic acid.

The effect of a rise of temperature on a chemical reaction is therefore of two kinds. In the first place, it increases the velocity of the reaction, and, in the second place, it alters the final state of equilibrium which is attained. This is well illustrated in the case of hydrogen and iodine, which has been very thoroughly investigated by Lemoine[1] and Bodenstein.[2] When these two elements are heated together at 290°, several weeks are required for the establishment of equilibrium, in which condition 16·37 per cent. of the total hydrogen is present in the free state; at 448°, on the other hand, the state of equili-

[1] *Ann. Chim. Phys.*, 1877 [5], **12**, 145.
[2] *Zeit. physikal. Chem.*, 1896, **13**, 56.

brium is reached in a few hours, 23·63 per cent. of the total hydrogen being free.

The exact extent to which the position of equilibrium is shifted by altering the temperature is given by the formula:— $\frac{d(\log_e K)}{dt} = -\frac{q}{RT^2}$, where K is the equilibrium constant of the reaction at the absolute temperature T, R is the gas constant, and q is the heat evolved when the reaction goes completely from left to right. The applicability of this formula has been tested, for instance, in connection with the equilibrium between sulphur trioxide, sulphur dioxide, and oxygen.[1]

Increase of pressure produces such a change in the position of equilibrium as is attended by a diminution of volume. Thus, when the external pressure on such a gas as nitrogen peroxide is increased, whilst the temperature is maintained constant, the dissociation of the gas is diminished, the combination of the NO_2 molecules being accompanied by a diminution of volume:

$$2NO_2 = N_2O_4.$$

This is shown by the following numbers obtained by E. and L. Natanson [2] at a temperature of 49·7°:—

Pressure.	Vapour density.
26·80 mm.	1·663
93·75	1·788
182·69	1·894
261·37	1·993
497·75	2·144

On the other hand, increase of pressure produces no change in the dissociation equilibrium of hydrogen iodide, the decomposition of this substance being unattended by any change in the number of molecules:

$$2HI \rightleftharpoons H + I_2.$$

[1] Bodenstein and Pohl, *Zeit. Elektrochem.*, 1905, **11**, 373.
[2] *Ann. Phys. Chem.*, 1885, **24**, 454; 1886, **27**, 656.

SPECTRUM ANALYSIS.

76 The following pages contain a short statement of the principles of spectrum analysis, and of the application of these principles to the detection of certain elementary and compound bodies. A complete treatise on spectrum analysis would be out of place here; for the subject has not only outgrown the space which can be assigned to it in a work like the present, but much diversity of opinion is still expressed on various important points, and a discussion of these views cannot be attempted here.[1]

Although the spectroscope has been employed for chemical investigations only since the year 1860, it has been the means of effecting some of the most striking discoveries of modern times. By its help the chemist is able to investigate the composition of terrestrial matter with a degree of exactitude previously undreamt of, and the discovery of the following new elementary bodies, as well as many members of the group of rare earths, indicates the importance of the spectroscope in chemical analysis:

Cæsium and Rubidium, by Kirchhoff and Bunsen.
Thallium, by Crookes.
Indium, by Reich and Richter.
Gallium, by Lecoq de Boisbaudran.
Helium, by Ramsay.

In addition to this, the application of the methods of spectrum analysis to the investigation of the nature of the light emitted by the heavenly bodies has opened out a completely new field of research, and has laid the foundations of a new science, that of *Celestial Chemistry*. Such has been the progress

[1] See Kayser, *Handbuch der Spectroscopie* (Hirzel, Leipzig, 1900–1912); Baly, *Spectroscopy* (Longmans, 1912); Watts, *Introduction to the Study of Spectrum Analysis* (Longmans, 1904).

made in this direction that not only are we now assured of the existence of many of our well-known terrestrial metals in the atmospheres of the sun and the fixed stars, but we have gained a knowledge of the physical condition of our luminary such as we formerly could not have thought possible, and have even been able to form a definite opinion concerning the physical and chemical constitution of the nebulæ and stars.

Moreover, it appears that the study of the spectrum is capable of leading to most interesting and important conclusions respecting the structure of the molecule, both at ordinary temperatures, and at the highest of which we have any knowledge. It seems probable also that spectrum observations will prove of great assistance in our endeavours to ascertain the structure of the atom and to trace the changes involved in its disintegration.

77 The principles upon which spectrum analysis is founded are simple enough. When any solid or liquid bodies are gradually heated they will all be seen to become luminous at some temperature. If the light which these bodies emit, when they begin to glow or become luminous, is examined by means of a prism and suitable optical arrangements, the rays of least refrangibility, viz., the red rays, are seen first, and, as the temperature rises, light of greater refrangibility is gradually emitted, until at last the body gives off blue or violet rays. When this point is reached the substance appears to the naked eye to be white-hot, as all the differently coloured rays, when brought together on the retina, produce the effect which we term white light. It is thus clear that the spectrum of every incandescent solid or liquid is the same, a bright continuous coloured band, the rays of which extend without a break through all the colours of the rainbow from red to violet.

With gases glowing at a high temperature, however, the case is quite different. The light which these bodies emit does not consist of light of all degrees of refrangibility. The spectrum of a glowing gas, instead of being continuous, is more or less broken up. Incandescent gases emit only rays of definite degrees of refrangibility, and their spectra consist, therefore, of bright lines, the position of which undergoes no change when the temperature is raised. Thus the vapour of sodium when incandescent emits a yellow light, and its spectrum consists of a double yellow line having wave-lengths of 5896 and 5890 ten-millionths of a millimetre, and being coincident with the dark lines in the solar spectrum termed by Fraunhofer the D lines. These two bright

sodium lines do not alter their position when the temperature of the vapour is raised; sodium vapour, as soon as it becomes luminous, glows with a yellow light, and by no rise of temperature can it be made white-hot. The peculiar colour of incandescent sodium vapour is best seen by fusing a small bead of sodium chloride on to the end of a fine platinum wire, and placing it in the non-luminous gas-flame. The salt volatilises, and the flame is coloured intensely yellow (Fig. 11).

78 Melville, in 1752, was the first to notice this yellow sodium flame, but he was unacquainted with its cause. In the year 1822, Brewster introduced his monochromatic lamp, the first idea being, however, due to Melville. In this

Fig. 11.

same year John Herschel investigated the spectra of many coloured flames, especially those obtained from the chlorides of copper and strontium, as well as from boracic acid, and in 1827 he writes concerning these observations—"the colour thus contributed by different objects to flame affords in many cases a ready and neat way of detecting extremely minute quantities of them." Again, Fox Talbot writes as follows in 1826 :—"The red fire of the theatres gave a most beautiful spectrum, with many lines or maxima of light. In the red these lines were more numerous and crowded, with dark spaces between them, besides an exterior ray greatly separated from the rest, and probably due to the nitre in the composition.

In the orange was one bright line, one in the yellow, three in the green, and several that were fainter." The extreme delicacy of the sodium reaction, and the universal distribution of this element, were facts unknown to Talbot, and he consequently attributes the yellow line first to sulphur, and afterwards to the presence of water. He adds, "if this opinion"—as to the cause of the production of the lines—"should prove correct, and applicable to the other definite rays, a glance at the prismatic spectrum of a flame might show it to contain substances which it would otherwise require a laborious chemical analysis to detect." In 1834 Talbot again writes :—"Lithia and strontia are two bodies characterised by the fine red tint which they communicate to the flame. Now it is very difficult to distinguish the lithia-red from the strontia-red by the naked eye, but the prism betrays between them the most marked distinction which can be imagined. The strontia flame exhibits a great number of red rays well separated from each other by dark intervals, not to mention an orange and a very definite bright blue ray. The lithia exhibits one single red ray. Hence I hesitate not to say that optical analysis can distinguish the minutest portions of these two substances from each other with as much certainty as, if not more than, any known method."

In the year 1845 Wm. Allen Miller published the results of experiments on the spectra of coloured flames, together with drawings, but owing to the fact that in these researches a luminous flame was made use of, the representations of the several spectra are wanting in clearness and individuality. Swan was the first to point out that the bright yellow line coincident with Fraunhofer's D, which was seen in every flame, is caused by the presence of sodium salts, and it is to him that we are indebted for the discovery of the extreme delicacy of the sodium reaction, and for the proof of the universal distribution of this element.

The earliest observations of the spectra of the metals which cannot be volatilised at the temperature of the non-luminous gas-flame were made in 1835 by Wheatstone. He allowed electric sparks to pass between poles of different metals, and found that the spectra of the sparks thus obtained were dissimilar. From this he concluded that the electric spark resulted from the volatilisation of the metal of the poles. "These differences," he says, "are so obvious, that one metal may easily

be distinguished from another by the appearance of its spark; and we here have a mode of discriminating metallic bodies more ready than that of chemical examination, and which may hereafter be employed for useful purposes."

In 1855 Ångström thoroughly investigated the nature of the electric spark, proving the important fact that the spark yields two superimposed spectra; one derived from the metal of the pole, and the other from the gas or air through which the spark passes.

The results obtained by the above-mentioned observers were, however, but little known, and the method was never applied to the solution of problems in analytical chemistry, until the year 1860, when Bunsen and Kirchhoff began their classical researches. It is to these two philosophers that we must in truth ascribe the discovery of the spectroscopic method, for they were the first to bring to bear upon this subject the sound principles of modern research, and to establish it upon the firm foundation of exact experiment.[1] Their labours soon met with reward. A new alkali metal (cæsium) was discovered almost immediately,[2] and the presence of various well-known metals in the solar atmosphere was at the same time ascertained beyond doubt.[3]

79 *Construction and use of the Spectroscope.*—The construction and arrangement of the spectroscope best suited to ordinary chemical purposes is shown in Fig. 12. This instrument consists of a prism (*a*) fixed upon a firm iron stand, and a tube (*b*) called a collimator, carrying the slit (*d*), seen on an enlarged scale in Fig. 14. Through this slit the rays from the coloured flame which is being examined (*e*) fall upon the prism, being rendered parallel by passing through a lens placed at the other end of the tube. The light, having been refracted by the prism (*a*), is received by the telescope (*f*), and the image is magnified before reaching the eye. The small luminous gas-flame (*h*, Fig. 12) is placed so as to illuminate a fixed scale contained inside the tube (*g*); this is reflected from the surface of the prism (*a*) into the telescope, and serves as a means of determining the position of the lines.

If, as is often the case, it is desired to observe two spectra

[1] Kirchhoff and Bunsen, "Chemical Analysis by Spectrum Observations," *Phil. Mag.*, [4], 1860, **20**, 89; 1861, **22**, 329, 498.

[2] *Berlin Akad. Ber.*, May 10, 1860; *Chem. News*, 1861, **3**, 132.

[3] *Berlin Akad. Ber.*, Oct. 27, 1859; *Phil. Mag.*, 1860, [4], **19**, 193.

simultaneously, so as to compare the position of the lines, this is effected by placing a small prism (*c*, Figs. 13 and 14) over one half of the slit. The rays from a second source of light

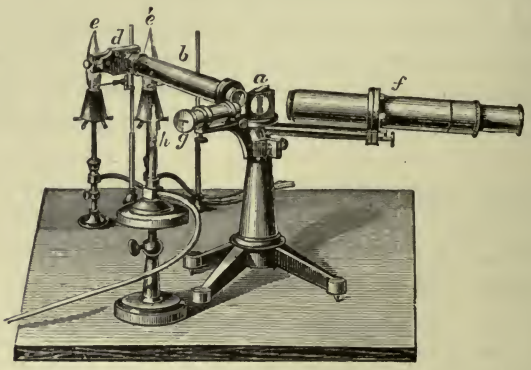


Fig. 12.

(*c'*, Fig. 12) may thus be brought into the collimator by internal reflection, so that of the two spectra produced, one occupies the upper half, and the other the lower half of the field of view.

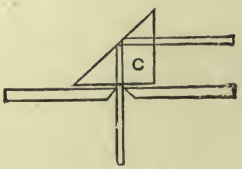


Fig. 13.

In spectroscopes adapted for more accurate measurements, the illuminated scale is discarded, and the telescope is made to move along a divided circle, by means of which the angular dispersion of the various lines may be measured.

Fig. 14.

Greater dispersion and separation of the lines is attained by the use of a series of prisms instead of a single prism (Fig. 15), which is a representation of the form of instrument used by Kirchhoff in his classical researches on the chemical composition

of the solar atmosphere. In such instruments the intensity of the light is much weakened, and they can therefore be used with advantage only when the source of light is of considerable intensity.

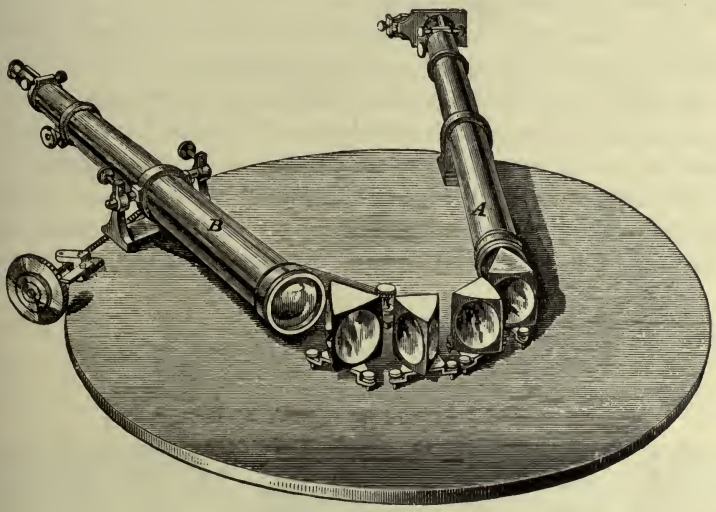


Fig. 15.

Greater accuracy in definition and wider dispersion are attained by the substitution of a diffraction grating, either plane or concave, for the prism, and such gratings, which usually contain from 5,000 to 20,000 lines perinch, are always employed for the most accurate work, when the source of light is of sufficient intensity.

METHODS OF PRODUCING EMISSION SPECTRA.

80 In order to obtain the peculiar spectrum of a chemical substance it is necessary to examine the light which the substance emits in a state of glowing gas. The method employed for this purpose differs according as the substance is solid, liquid, or gaseous.

81 *Flame-Spectra.*—Slightly volatile substances, such as the salts of the metals of the alkalis and alkaline earths, may be placed upon a fine platinum wire, and this is then brought into the non-luminous Bunsen flame. The salts there volatilise, the

flame assumes a characteristic colour, and this coloured flame, when examined by the spectroscope, exhibits the peculiar spectrum of the given substance. Apparatus specially adapted for the continuous introduction of salts into the Bunsen flame, has been described by Beckmann.[1]

Many substances which yield no bright line spectra in the Bunsen flame do so in the oxy-hydrogen flame.

82 *Arc- and Spark-Spectra.*—When the substance is non-volatile at the temperature of the non-luminous flame, as is the case with most metals, and requires a much higher temperature to convert it into gas, either a powerful electric spark or the electric arc must be employed. The arrangement used for obtaining the spectra of metals by means of the electric spark

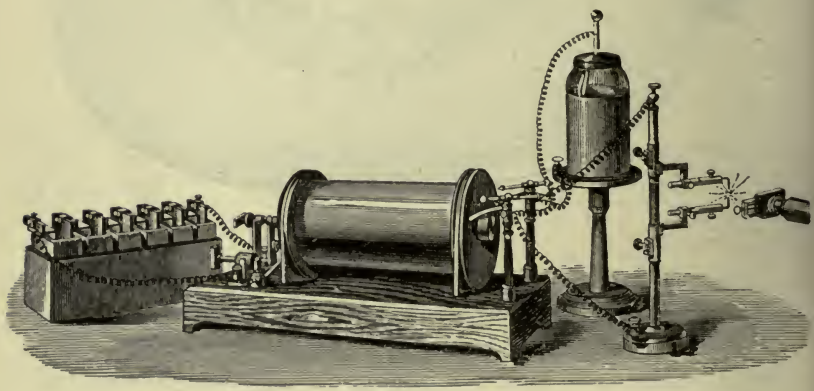


Fig. 16.

is seen in Fig. 16. It is only necessary to allow a powerful and bright spark to pass between poles made of the metal in question to obtain the characteristic bright-line spectrum of the metal, although it is to be remembered that the bright lines of the gases through which the spark passes (the air lines) will likewise be observed.

Another method of examining spark-spectra with especial regard to the easy chemical detection of the difficultly volatile metals was proposed by Bunsen.[2] The spark passes between two small cones of pure porous carbon, these having been impregnated with a solution of a pure compound of the metal under examination. The advantage of this spark-spectrum

[1] *Zeit. physikal. Chem.*, 1907, **57**, 641.
[2] *Phil. Mag.*, 1875, [4], **50**, 418, 527.

method is well shown in the case of the detection of the allied rare metals cerium, lanthanum, praseodymium, and neodymium; yttrium and erbium. The chlorides of these metals do not volatilise at the temperature of the non-luminous flame, but yield well-defined and characteristic spark-spectra by which they can be recognised without difficulty.

Another method which is of special value in observing the spectra given by the soluble salts of the metals has been perfected by Lecoq de Boisbaudran. It consists in connecting the solution of the salt with the negative wire from the induction coil, and then passing the spark from a positive pole of platinum placed just above the surface of the liquid. This method has proved of great value in the examination of the compounds of rare earths.

For arc-spectra the ordinary arc between carbon points is used, the substance to be examined being placed on the positive pole, or packed in a hole bored along the axis of the carbons.

Fig. 17.

In the case of metals, the poles may be made of the metal itself.

If the substance is a gas at the ordinary temperature the gaseous particles can be made to glow, and then to emit the rays which are peculiar to them, by passing an electric discharge through the gas. The colour of the electric spark or discharge will then be found to vary according to the nature of the gas, and a spectroscopic examination of the light then emitted reveals the characteristic spectrum of the gas. The examination of the spectra of gases at low pressures is effected by means of *Geissler's Tubes* (Fig. 17). These contain the gases in a highly rarefied condition, and are furnished with platinum or aluminium wires fused into the glass. As the rarefied gases offer little resistance to the passage of the electricity, the discharge passes readily through a long narrow tube, heating up the particles of gas, and thus producing a brightly luminous column. The vapours of liquids which are easily volatilised can also be examined in this way.

The spectra of gases at the ordinary pressure, or under increased pressure, can be observed by passing a spark (as described above) between metal poles in an atmosphere of the gas at the required pressure. It must be remembered that in such experiments the lines due to the metallic poles are also seen.

Phosphorescence spectra are shown by many substances when they are exposed to the cathode discharge in a highly exhausted glass bulb (Crookes). This method has been much used for the examination and characterisation of the rare earths.

When the invisible portions of the spectrum are to be examined it must be remembered that glass is much less transparent to the infra-red rays than to ordinary light, and is almost opaque to the ultra-violet rays. These last are, however, transmitted by quartz prisms and lenses, and then can be photographed, or rendered visible by means of a screen coated with some phosphorescent substance such as platinocyanide of barium or potassium. The infra-red spectrum is best obtained by means of a metallic diffraction grating.

MAPPING AND MEASURING SPECTRA.

83 The following method of mapping spectra as observed with a spectroscope provided with an illuminated scale, was proposed by Bunsen as a convenient mode of recording the position, breadth, and intensity of the lines constituting the various spectra. "For the purpose of facilitating the numerical comparison of the data of various spectrum observations, we give in Fig. 18 graphical representations of the observations which are taken from the guiding lines given in the chromo-lithograph drawings of the spectra published in our former memoirs, and in which the prism was placed at the angle of minimum deviation. The ordinate edges of the small blackened surfaces, referred to the divisions of the scale as abscissæ, represent the intensity of the several lines, with their characteristic gradations of shade. These drawings were made when the slit was so broad, and the flame of such a temperature, that the fine bright line upon the broad Ca α band began to be distinctly visible.

"This breadth of the slit was equal to the fortieth part of the distance between the sodium line and the lithium line α.

For the sake of perspicuity, the continuous spectra which some bodies exhibit are specially represented on the upper edge of the scale, to the divisions of which they are referred as abscissæ."

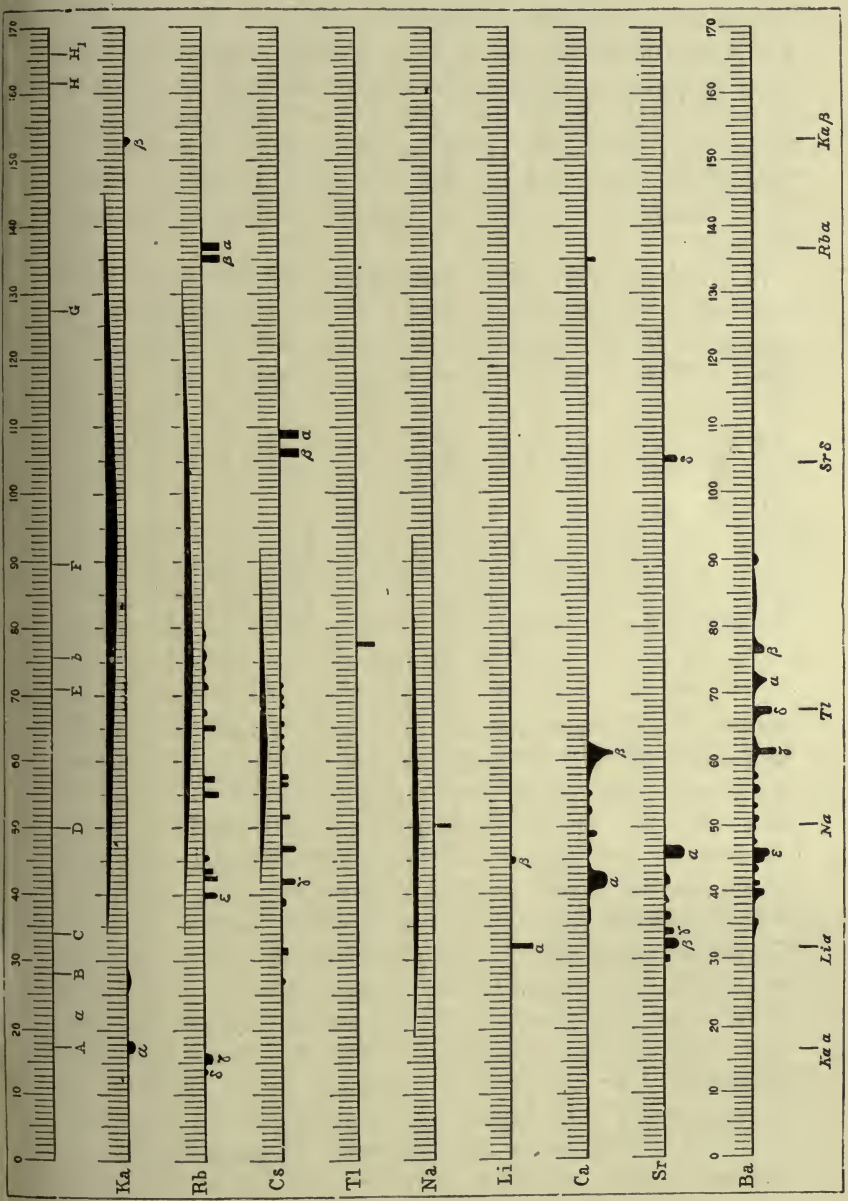


FIG. 18.

The positions of the lines in a spectrum are now generally recorded in terms of their *wave-lengths*, which are usually expressed in ten millionths of a millimetre (1×10^{-7} millimetre), a unit of measurement which is known as Ångström's unit (A.U.), or as a "tenth metre," since it equals 1×10^{-10} metre. Wave-lengths are, however, sometimes expressed in terms of $\mu = 0{\cdot}001$ millimetre, or of $\mu\mu = 0{\cdot}000001$ millimetre. For many purposes it is more convenient to deal with the oscillation frequency of the ray, *i.e.*, the number of waves in a given unit of length, the centimetre being usually chosen. Thus, the less refrangible yellow sodium line has the wave-length 5896·2 A.U. (589·62 $\mu\mu$; 0·58962 μ), and the oscillation frequency 16960·1.

In order to ascertain the wave-lengths of the various lines observed, it is necessary to draw a curve which represents the dispersion of the particular instrument which is being employed. This is done by selecting a number of lines as

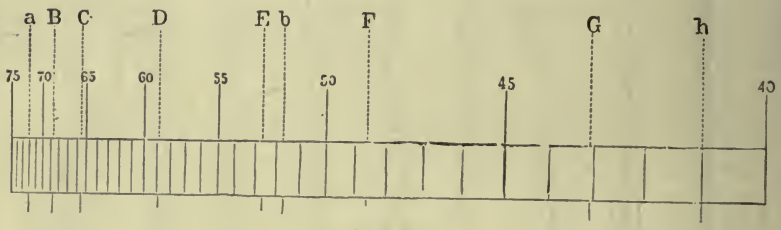


FIG. 19.

standard lines, and plotting the wave-lengths of these as ordinates, and their positions on the scale of the instrument as abscissæ. The curve joining the points thus obtained can then be used for determining the wave-length of a line observed at any position on the scale. Precisely the same process may be carried out with the oscillation frequencies.

Some instruments are provided with illumination scales, divided and numbered so as to permit of the direct determination of the wave-length for any region of the visible spectrum. Such scales are similar to that shown in Fig. 19, and give wave-lengths in $\mu\mu$, in accordance with the determinations of Ångström. The divisions of the scale enable the observer to read directly to the second significant figure, and to estimate the third. Such scales are sufficiently accurate for ordinary qualitative work but can be employed only with a prism of the

same dispersive power as that for which they have been constructed.

The most accurate method of recording the spectrum given by any substance is to allow the image of the spectrum to fall upon a photographic plate, contained in a holder fitting into a camera which replaces the eye-piece of the telescope. The great advantage of the photographic method is that it is thus possible to determine with great accuracy the positions of a much larger number of lines than can be done by mere observations with the eye, very faint lines being recorded when the time of exposure is increased. This is shown by the fact that in the portion of the spectrum between wave-lengths 3900 and 4100, the number of lines of twelve metals noted by Lockyer is 416, as against 39 lines observed by Thalén. The photographic method can, moreover, be extended to those portions of the spectrum which are invisible to the eye.

If the spectrum of some standard substance is photographed on the same plate as the spectrum to be examined, the unknown wave-lengths of the new lines can readily be determined by interpolation from the known wave-lengths of the lines of the standard substance.

It has been found possible to photograph the spectrum between wave-lengths 20000 A.U. in the infra-red and 1000 A.U. in the ultra-violet, but very special methods are required to obtain records beyond the interval 9000–2100. In the infra-red, measurements may be made also by means of the bolometer, an instrument devised by Langley, which detects the heating effect of the rays by the change of resistance produced in a thin metallic wire. By the use of this instrument radiations of wave-length 1,000,000 A.U. (0·1 mm.) have been detected.

84 *Variations observed in Spectra.*—The nature of the spectrum emitted by a gas depends upon the temperature and pressure to which the gas is subjected. When an electric discharge of low intensity is passed through a highly rarefied gas, in a Geissler tube, the spectrum usually consists of a series of broad bright bands, which are made up of a great number of very fine lines crowded closely together; this is termed a "channelled" spectrum (Plücker). The band spectrum of the discharge in the neighbourhood of the positive pole is, moreover, often different from that near the negative pole. At a higher temperature, produced by a discharge of greater intensity, the spectrum consists of bright lines. Finally, when the pressure is increased, under

certain conditions, many gases are found to give continuous spectra.

These variations are well exemplified by the cases of oxygen and nitrogen, the former of which gives no fewer than seven different spectra, among which are included the absorption spectra of both oxygen and ozone.

Argon, krypton, and xenon behave in a somewhat different manner from the foregoing gases, yielding two distinct bright line spectra according as the ordinary discharge or the jar discharge is employed.

Further, it is often found that variation in the pressure of the gas, or the intensity of the discharge, produces a variation in the relative intensity of the lines of the spectrum. Thus, in helium at a pressure of 7—8 mm., the yellow lines are the most conspicuous, and the gas glows with a yellow light; whilst at a lower pressure, the most conspicuous line is in the green, and the gas glows with a greenish coloured light.

The cause of these variations is at present unknown. It appears probable, however, that the characteristic spectrum of each element is due to the vibrations of the corpuscles which are present in its atoms (p. 40), rather than to the vibrations of the atom as a whole, so that a change in the spectrum corresponds to some alteration in the mode of vibration of some or all of the corpuscles making up the atom.[1]

THE SPECTRA OF THE ELEMENTS.

85 If we compare the spectra of the various elements, obtained according to one or other of the above methods, we find that each element yields a characteristic spectrum, consisting of a larger or smaller number of bright lines, and that no two elements have even a single line in common.

These lines do not undergo any alteration in relative position, or in degree of refrangibility, when the temperature is raised. The double sodium line D is always seen at the same position of the spectrum, viz., wave-lengths 5896 and 5890, to whatever temperature the vapour may be raised. The *number* of lines visible in any given spectrum, as well as their relative

[1] See J. J. Thomson, "Some applications of the theory of electric discharge through gases to Spectroscopy," *Nature*, 1906, **73**, 495; compare Stark, *Physikal. Zeit.*, 1908, **9**, 85.

intensities, may, on the contrary, undergo considerable changes dependent upon the temperature of the glowing gas, the pressure to which it is subjected, and the thickness of the incandescent layer. Thus, for example, the spectrum of lithium, as obtained by placing some salt of the metal in a non-luminous gas-flame, consists of one very bright red line, α, wave-length 6708, and a very faint orange line, β, wave-length 6104 (Fig. 20). If, however, the spectrum of lithium obtained by placing one of its salts in the electric arc, or even in the oxyhydrogen flame, is examined, a new and splendid blue line (γ), wave-length 4602, makes its appearance, along with several others of less intensity, making in all twenty lines. The same phenomenon is observed in the case of the strontium spectrum (Fig. 20), where no fewer than four new lines (ϵ, η, κ, and λ)

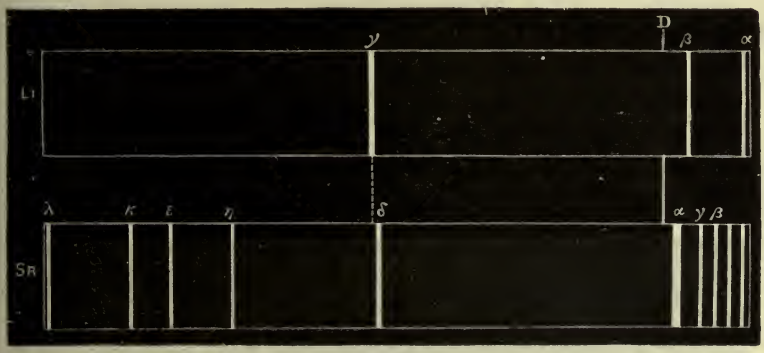


Fig. 20.

make their appearance on raising the temperature of the incandescent vapour of the metal.

A very important feature of the spark spectra of the metals was first observed by Lockyer, making use of a method in which the image of the electric arc formed by the incandescence of the metal was projected by a lens on the slit of the spectroscope. By this process he was enabled to examine the spectrum of various portions of the arc, and was thus led to the remarkable discovery that in each metallic spectrum certain lines are not only brighter than others, but are also *longer* than the rest. That is, one line of a given metal is seen to stretch across from pole to pole, whilst another line appears only in the neighbourhood of the poles, where the temperature is highest and the density of the incandescent gas may be supposed to be greatest.

The longest lines are the ones which exist in the spectrum produced at lower temperatures.

The application of instruments possessing greater powers of resolution to the study of the spectrum has shown that the great majority of the bright lines observed in the spectra of the elements are in reality composed of a number of separate lines differing only very slightly in wave-length, but often varying considerably in intensity. Thus, the red line of hydrogen consists in reality of two lines of unequal brightness, differing in wave-length by only 0·14 A.U. Again, the green line of thallium is triple, and certain of the lines of mercury quadruple.

THE SPECTRA OF COMPOUNDS.

86 It appears probable that every individual compound possesses a characteristic spectrum which consists of broad bands, and not of lines like the spark spectrum of an element. It is, however, impossible in many cases to observe this, because the compound is decomposed before it reaches a sufficiently high temperature to produce a spectrum. Thus, when the compounds

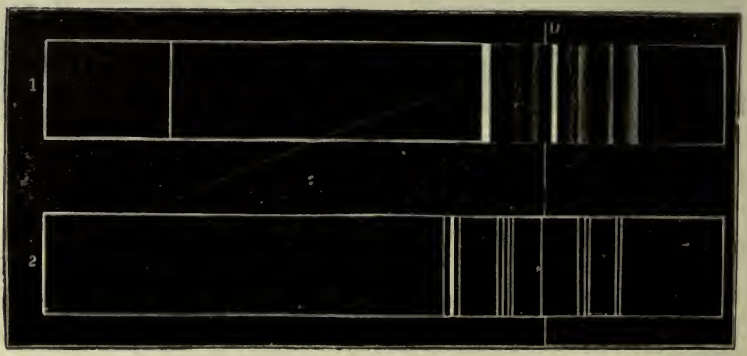


Fig. 21.

of one of the alkali metals are introduced into a Bunsen flame, the spectrum produced is the same whatever compound is used, and consists of lines which are all found in the spark spectrum of the metal. On the other hand, the different salts of barium, calcium, or strontium yield different spectra, and these, moreover, scarcely contain a single line which occurs in the actual spectrum of the metal. Thus, if a bead of calcium chloride is

brought into the flame a reddish tint is observed, caused by the volatilisation of the salt. The spectrum of this coloured flame consists of a series of differently coloured broad bands, the positions of which are indicated in No. 1, Fig. 21, and which are mainly due to the unaltered chloride and the oxide formed from it by calcination. If, now, the same bead is placed between two metallic poles, and a bright electric spark is allowed to strike round the bead, the spark is seen to assume a bright-red tint, and when this coloured spark is observed by means of a spectroscope a spectrum of fine bright lines, shown in No. 2, Fig. 21, is seen. In the first instance, the spectrum is that of a calcium compound; in the second, it is that of the metal itself.

RELATIONS BETWEEN SPECTRAL LINES.

87 *The Spectrum of a given Element.*—It appears from the work of Liveing and Dewar, Hartley, and especially of Balmer, Rydberg, Schuster, and Kayser and Runge [1], that relations exist between the wave-lengths of the lines in the spectrum of a given element. In the spectra of many elements certain series of lines have been found, the wave-lengths of which can be expressed as functions of a series of whole numbers.

Kayser and Runge employ the formula,

$$\frac{1}{\lambda} = A - Bn^{-2} - Cn^{-4},$$

in which λ is the wave-length, A, B, and C are constants determined from the observations, and n takes the values of successive whole numbers.

Rydberg [2], on the other hand, proposes the more rational equation,

$$n = n_o - \frac{109675}{(m + \mu)^2},$$

in which m takes the value of successive whole numbers, n is the oscillation frequency expressed as the number of waves per centimetre, μ is a constant characteristic of the special

[1] *Journ. Chem. Soc.*, 1883, **43**, 390; *Phil. Trans.*, 1883, **174**, 187; *Nature*, 1895, **52**, 106; *British Assoc.*, 1888, 1895; *Ann. Physik*, 1894, **52**, 114.

[2] *K. Svenska Vetensk. Akad. Hand.*, 1890, **23**, No. 11.

series, and n_o is the value of n when m becomes infinite; n_0 is thus the theoretical limit of the series, and is termed the *convergence frequency*. Series of this kind were first discovered in the spectrum of hydrogen by Balmer,[1] but they are best exemplified by the spectra of the alkali metals, all of which appear to be of the same type. Thus, the arc-spectrum of sodium may be regarded as consisting of a large number of pairs of lines, and among these there have been detected three series each consisting of paired lines. The first of these is called the *principal series*, because it contains the most important and conspicuous lines of the spectrum. It consists, in the case of sodium, of numerous pairs of lines, the frequency difference between the members of the pairs becoming smaller as the frequency increases, so that the members of the pairs are closer together in the ultra-violet than in the visible spectrum.

The second is called the *first subordinate series*, or since the lines are diffuse, the *nebulous* series; it consists of a number of pairs, with a constant frequency difference of 17·2 between the members of the pairs. The third is called the *second subordinate series* or the *sharp* series; the lines are sharply defined, and there is a constant frequency difference of 17·2 between the pairs.

The equations given by Rydberg for the less refrangible line of the pairs in these three series are:

$$\text{Principal series} \quad n = 41452{\cdot}61 - \frac{109675}{(m + 1{\cdot}116329)^2}$$

$$\text{Nebulous series} \quad n = 24470{\cdot}13 - \frac{109675}{(m + 0{\cdot}64984)^2}$$

$$\text{Sharp series} \quad n = 24470{\cdot}13 - \frac{109675}{(m + 0{\cdot}988436)^2}.$$

In the principal series the more refrangible lines of the pairs are given when $\mu = 1{\cdot}117072$; in the other series μ remains constant, but the convergence frequency for the second line of the pair is greater by 17·2.

These formulæ indicate that the two subordinate series have the same convergence frequency, and further bring out a relation of great importance between the principal series and the subordinate series, which is known as the Rydberg-Schuster law.

[1] *Ann. Physik*, 1885, **25**, 80.

having been independently discovered by these two observers. This consists in the fact that the frequency of the first line of the principal series is equal to the difference between the convergence frequencies of the principal and subordinate series. Thus in the case of sodium this difference is 41452·61—24470·13 = 16982·48, and this number is the oscillation frequency of the less refrangible D line (wave-length 5896·16). Other relations also exist which clearly indicate that these three series are closely related to each other and are not represented merely by independent empirical formulæ.[1]

Similar relations are found in the spectra of the other alkali metals. In the spectra of the metals magnesium, calcium, strontium, zinc, cadmium, and mercury, the principal series are wanting, or only very scantily represented, but in all these cases the nebulous and sharp series have been found, each composed of triplets of lines instead of the pairs present in the spectra of the alkali metals. It must be remembered that, as a rule, the spectrum contains also many lines which do not fall into these series.

In other cases, such as tin, lead, arsenic, antimony, bismuth, &c., no series have been discovered, but numerous groups of lines of constant frequency difference have been observed. Attempts have been made to connect the existence of these various relations between the lines of a spectrum with the mode of vibration and form of the atom, but no very definite success has yet been attained.[2]

88 *The Spectra of Allied Elements.*—Relations also undoubtedly exist between the spectra of allied elements, and this is well seen in the case of the alkali metals. The resemblance between these spectra was first noticed by Lecoq de Boisbaudran in 1869, the general effect being a shifting of the lines towards the red as the atomic weight increases. Ramage[3] has carried the matter somewhat further by showing that the oscillation frequencies of the corresponding lines in the series found in the spectra of potassium, rubidium, and cæsium, bear a simple relation to the squares of the atomic weights of the metals. A somewhat similar relation has been

[1] For recent work on spectral series, see Hicks, *Phil. Trans.*, *A*, 1909, **210**, 57 ; 1912, *A*, **212**, 33 ; also *Œuvres de Walther Ritz* (Gauthier-Villars ; Paris, 1911).

[2] See Lindemann, *The Monist*, Jan., 1906, and *Nature*, 1906, **73**, 392.

[3] *Proc. Roy. Soc.*, 1902, **70**, 1,303.

brought out by Marshall Watts,[1] who has indicated that the atomic weight of a metal, such as zinc, may be calculated from a comparison between its spectrum and that of an allied metal of known atomic weight, such as cadmium. Such a calculation is based on the fact that the differences between the oscillation frequencies of corresponding lines in the two spectra are in the ratio of the squares of the atomic weights of the metals. Thus taking the following pairs of corresponding lines,

Cadmium.		Zinc.	
30654·4	diff. 1251·1,	32500·0	diff. 428·7,
31905·5		32928·7	

we have $$\frac{1251{\cdot}1}{428{\cdot}7} = \frac{(111{\cdot}83)^2}{(65{\cdot}4)^2}.$$

Our knowledge of the whole question of the relations between the separate lines of a spectrum, and between the spectra of different elements, is still in a very rudimentary state, although the question is one of the most interesting in the whole field of chemical and physical inquiry.

APPLICATION OF THE SPECTROSCOPE TO CHEMICAL ANALYSIS.

89 This instrument is especially valuable in ordinary qualitative analysis for the detection of the metals of the alkalis and alkaline earths, and of the more recently discovered metals, thallium, indium, and gallium, inasmuch as the salts of all these metals can be volatilised in the non-luminous gas-flame. The following extract from Bunsen and Kirchhoff's memoir (1860) on this subject gives some idea of the ease and accuracy with which the presence of certain of these metals can be detected, and leads to the conclusion that the sodium salts are universally distributed:

"The following experiment shows that the chemist possesses no reaction which in the slightest degree will bear comparison as regards delicacy with this spectrum analytical determination of sodium. In a far corner of our experiment room, the capacity of which was about sixty cubic metres, we burnt

[1] *Phil. Mag.*, 1903, **5**, 203. For application of this relationship in calculating the atomic weight of radium, see Runge and Precht, *Phil. Mag.*, 1903, **5**, 476; Watts, *ibid.*, 1909, **18**, 411.

a mixture of three milligrams of chlorate of sodium with milk sugar, whilst the non-luminous colourless flame of the lamp was observed through the slit of the telescope. Within a few minutes, the flame, which gradually became pale yellow, gave a distinct sodium line, which, after lasting for ten minutes, entirely disappeared. From the weight of sodium salt burned and the capacity of the room, it is easy to calculate that in one part by weight of air there is suspended less than $\frac{1}{20,000,000,000}$ of a part of soda smoke. As the reaction can be observed with all possible comfort in one second, and as in this time the quantity of air, which is heated to ignition by the flame, is found to be only about 50 cub. cent., or 0·0647 gram of air, containing less than $\frac{1}{20,000,000,000}$ of sodium salt, it follows that the eye is able to detect with the greatest ease quantities of sodium salt less than $\frac{1}{3,000,000}$ of a milligram in weight. With a reaction so delicate, it is easy to understand why a sodium reaction is almost always noticed in ignited atmospheric air. More than two-thirds of the earth's surface is covered with a solution of chloride of sodium, fine particles of which are continually being carried into the air by the action of the waves. These particles of sea-water, cast thus into the atmosphere, evaporate, leaving almost inconceivably small residues which, floating about, are almost always present in the air, and are rendered evident to our eyes in the sunbeams. These minute particles perhaps serve to supply the smaller organised bodies with the salt which larger animals and plants obtain from the ground. In another point of view, however, the presence of this chloride of sodium is of interest. If, as is scarcely doubtful at the present time, the explanation of the spread of contagious disease is to be sought for in some peculiar contact action, it is possible that the presence of so antiseptic a substance as chloride of sodium, even in almost infinitely small quantities, may not be without influence upon such occurrences in the atmosphere.

"By means of daily and long-continued spectrum observations it would be easy to discover whether the alterations of intensity in the line Naα produced by the sodium in the air have any connection with the appearance and the direction of march of an epidemic disease.

"The unexampled delicacy of the sodium reaction explains also the well-observed fact, that all bodies after a lengthened

exposure to the air show the sodium line when brought into a flame, and that it is only possible in a few salts to get rid of the line even after repeated crystallisation from water which has been in contact with platinum only. A thin platinum wire freed from every trace of sodium salt by ignition shows the reaction most visibly on allowing it to stand for a few hours in the air; in the same way the dust which settles from the air in a room shows the bright line Naα. To render this evident it is only necessary to knock a dusty book, for instance, at a distance of some feet from the flame, when a wonderfully bright flash of the yellow band is seen."

In like manner the metal lithium before the year 1860 was known to exist only in a few rare minerals. It is now ascertained that lithium compounds are most widely distributed, occurring not only in every mineral spring, but in river and sea-water, in the juices of almost every plant, and even in human blood and muscular tissue.

Again, to quote from Bunsen's Memoir: "Minerals containing lithium, such as triphylline, triphane, petalite, and lepidolite require only to be held in the flame in order to obtain the bright line in the most satisfactory manner. In this way the presence of lithium in many felspars can be directly detected as, for instance, in the orthoclase from Baveno. The line is only seen for a few moments, directly after the mineral is brought into the flame. In the same way the mica from Altenburg and Penig was found to contain lithium, whereas micas from Miask, Aschaffenburg, Modum, Bengal, Pennsylvania, &c., were found to be free from this metal. In natural silicates which contain only small traces of lithium this metal is not observed so readily. The examination is best conducted as follows: a small portion of the substance is digested and evaporated with hydrofluoric acid or fluoride of ammonium, the residue moistened with sulphuric acid and heated, the dry mass being dissolved in absolute alcohol. The alcoholic extract is then evaporated, the dried mass again dissolved in alcohol, and the extract allowed to evaporate on a shallow glass dish. The solid pellicle which remains is scraped off with a fine knife, and brought into the flame by the thin platinum wire. For one experiment $\frac{1}{10}$th of a milligram is in general quite a sufficient quantity. Other compounds besides the silicates, in which small traces of lithium require to be detected, are transformed into sulphates by evaporation with

sulphuric acid or otherwise, and then treated in the manner described.

"In this way we arrive at the unexpected conclusion that lithium is most widely distributed throughout nature, occurring in almost all bodies. Lithium was easily detected in forty cubic centimetres of water of the Atlantic Ocean, collected in 41° 41′ N. latitude and 39° 14′ W. longitude.

"Ashes of marine plants (kelp) driven by the Gulf Stream on to the Scottish coasts contain evident traces of this metal. All the orthoclase and quartz from the granite of the Odenwald which we have examined contains lithium. A very pure spring water from the granite in Schleierbach, on the west side of the valley of the Neckar, was found to contain lithium, whereas the water from the red sandstone which supplies the Heidelberg laboratory was shown to contain none of this metal. Mineral waters, in a litre of which lithium could hardly be detected according to the ordinary methods of analysis, gave the line Li*a* even if only a drop of the water on a platinum wire were brought into the flame. All the ashes of plants growing in the Odenwald on a granite soil, as well as Russian and other potashes, contain lithium.

"Even in the ashes of tobacco, in vine leaves, in the wood of the vine and in the grapes, as well as in the ashes of the crops grown on the Rhine plains near Wäghausel, Deidesheim, and Heidelberg, on a non-granite soil, was lithium found. The milk of the animals fed on these crops also contains this widely diffused metal."

90 *Discovery of New Elements.* The discovery by Bunsen of two new alkali metals in the mineral water of Dürkheim,[1] was one of the first results of the application of the spectroscope to chemical analysis. Both these new elements are contained in the mineral water in extremely small quantities, so that 44,000 kilos. of the water had to be evaporated in order to obtain 16·5 grams of the mixed chlorides. The first of these new metals yields a spectrum distinguished by two splendid bright blue lines, and hence the name *Caesium* (*caesius*, the blue colour of the sky) was given to it. The second new metal is characterised by a spectrum which contains a bright red line, less refrangible than the potassium line K*a*, and also a line in the violet. As the red line is the one by which the presence of this metal can be most readily and certainly

[1] For an analysis of this water see Vol. I., p. 326.

detected, Bunsen gave to it the name of *Rubidium* (*rubidus*, dark-red).

Since this discovery in 1860, chemists have recognised the presence of both these metals in very varied situations; one of them, rubidium, being comparatively widely distributed, and found in very many mineral waters. Thus, for example, the celebrated water of Bourbonne-les-Bains contains 0·032 gm. of cæsium chloride, and 0·010 gm. of rubidium chloride in one litre of water; whilst in the well-known springs of Vichy, Gastein, Nauheim, Karlsbrunn, and many more, either one or both of these new metals have been discovered. Rubidium has been found to be more widely diffused than cæsium, occurring in animate as well as in inanimate nature. It has been found in beetroot, in tobacco, in the ash of the oak (*Quercus pubescens*), in coffee, in tea, and in cocoa.

In their general chemical characters, as in their spectroscopic relations, these two new metals exhibit the closest analogy with potassium. So much so is this the case, that without the aid of the spectroscope, and the differences which the spectra of these three metals present, it was absolutely impossible to distinguish between them. Chemists had, in fact, experimented upon cæsium but had mistaken it for potassium. (See under Cæsium.)

Soon after the discovery of the new alkali metals by Bunsen, Crookes, in 1861, proved the presence of a new metal in a seleniferous deposit from a sulphuric acid chamber at Tilkerode in the Harz. To this new element he gave the name of *Thallium*, from *thallus*, a young twig, owing to the bright green colour which this substance and its compounds impart to the non-luminous flame. The spectrum of thallium is a simple one, consisting of one bright green line (Tl*α*), with a wave-length of 5349. Thallium has since been shown to occur frequently in iron pyrites and several other minerals, so that it is a somewhat widely distributed element. It exhibits very remarkable and interesting chemical properties, since in certain respects it closely resembles the metals of the alkalis, whilst in others it more nearly approaches the heavy metal lead. Hence thallium was very appropriately termed by Dumas the ornithorhynchus amongst the metals.

A fourth new metal was discovered in the year 1864, by Reich and Richter, in Freiberg. They gave to this substance the name of *Indium*, owing to the fact that it imparts a dark-blue or indigo

tint to the flame, and its spectrum consists of two indigo-coloured lines. It has been found, although in small quantities only, in the zinc blendes from Freiberg, Goslar, and a few other places.

In 1875, Lecoq de Boisbaudran found another new metal in zinc blendes from the Pyrenees. To this substance he gave the name of *Gallium*. Its spectrum consists of two violet lines, which are best seen in the arc spectrum. The brightest of these lines has a wave-length of 4172, the second line having a wave-length of 4033.

The application of spectrum analysis to the study of the rare earths has made us acquainted with a very large number of new substances, among which may be mentioned scandium, ytterbium, and samarium, although it is not yet certain that all these are individual substances. Of surpassing interest is Ramsay's discovery of helium (1895) in the gas evolved by the action of sulphuric acid on clèveite, a rare uranate of uranyl, lead, and the rare earths. The gas evolved in this reaction was supposed by certain observers to be nitrogen, but examination showed that its emission spectrum differed entirely from that of nitrogen, and was characterised by a double yellow line of wave-length 5876 which occupies the same place in the spectrum as a double dark line in the solar spectrum. This solar line had been observed previously, and since it did not coincide with a bright line of any known element, had been ascribed by Lockyer to an element, which he named helium, since it occurred in the sun but not in the earth. Further investigations have shown that the gas in question contains this solar element, which is present also in the terrestrial atmosphere (Vol. I., p. 931).

ABSORPTION SPECTRA.

91 In accordance with the important optical law known as the law of exchanges, every incandescent body is capable of absorbing, at the same temperature, exactly those kinds of rays which it emits. Hence a glowing body which yields a continuous spectrum exhibits, at the same temperature, a continuous absorption, whilst those bodies the emission spectra of which are broken or discontinuous yield, under similar conditions of temperature, absorption spectra which are in like manner broken or discontinuous. This selective absorptive

action of glowing gases is strikingly shown in the case of sodium vapour. If a small piece of this metal is burnt in an iron cap in front of the slit of the spectroscope the bright yellow sodium lines will at first be seen (No. 2, Fig. 22), but they will soon be replaced by two dark lines which are exactly coincident with the bright yellow lines, and are seen upon a background of a bright continuous spectrum (No. 1, Fig. 22). The sodium spectrum has thus been *reversed*, inasmuch as the yellow rays in passing through the sodium vapour have been absorbed, whilst the particles of glowing oxide of the metal yield a continuous spectrum. Sodium vapour is opaque to the yellow D rays. In a similar way the bright lines of the emission spectra of lithium, calcium, strontium, barium, as well as of magnesium, copper, and several other heavy metals, have been reversed, or the absorption spectra of these metals have been

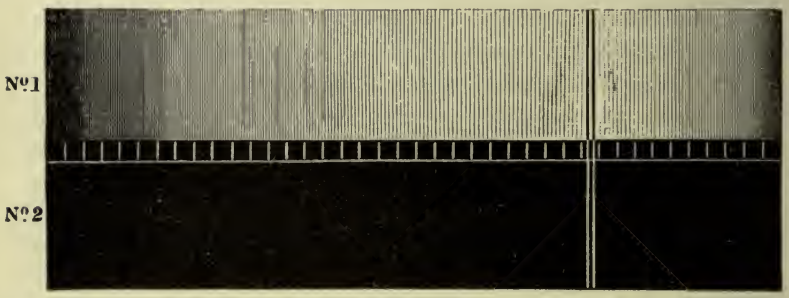


Fig. 22.

obtained. The numerous fine black lines seen in the solar spectrum, and known as *Fraunhofer's lines*, are produced by the reversal of the spectra of hydrogen, sodium, calcium, iron, magnesium, and other metals which are present in the state of luminous gas in the solar atmosphere.

This selective absorption is exhibited by nearly all substances in some portions of the spectrum, although in many cases it is confined to the non-visible region. The dark absorption bands seen when white light passes through the vapour of iodine (No. 1, Fig. 23), and those first observed by Brewster in the red fumes of nitrogen peroxide (No. 2, Fig. 23), are good examples of this selective absorptive power of gases. Even some colourless gases, such as aqueous vapour, possess a strong power of selective absorption when a column of sufficient depth is examined (Rain-band)

In addition to the production of bands and lines, there is often a general absorption, extending over a considerable extent of the spectrum. The measurement of the exact position, extent, and character of the absorption bands is a matter of considerable difficulty, since they are often diffuse, with badly defined

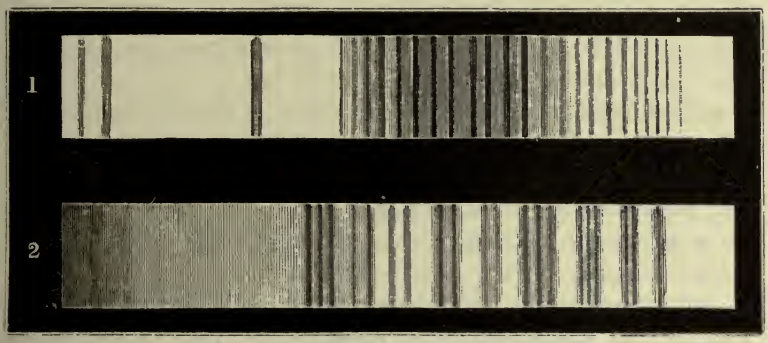


Fig. 23.

edges. In such cases the position of maximum absorption must be found by photometric measurement, and a series of observations must be made on different thicknesses of the substance in order to ascertain how the bands vary in intensity and extent.

The arrangement shown in Fig. 24 is one which may be used

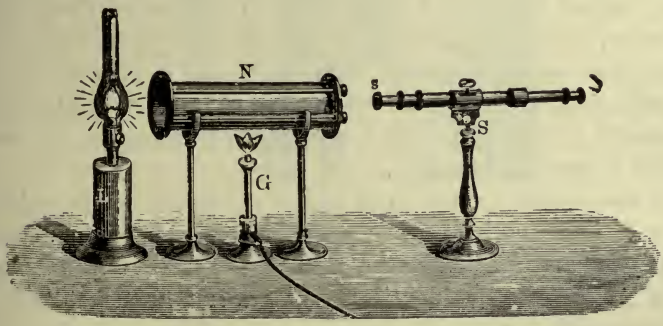


Fig. 24.

for examining the absorption spectra of gases by means of a direct-vision spectroscope.

The absorption spectrum of a substance, when examined at a lower temperature than that at which the bright line spectrum is obtained, is not, as a rule, identical with the emission spectrum. Thus the dark absorption lines seen in chlorine are not identical

with, or even analogous to, the bright lines of the emission spectrum of chlorine.

The dark absorption bands of iodine, on the other hand, correspond with the emission band spectrum obtained at a low pressure in a Geissler tube and also in the flame.

Characteristic absorption spectra are shown in the visible region also by coloured liquids and solutions, whilst many liquids which appear perfectly colourless produce selective absorption in the ultra-violet or infra-red.

92 According to the theory of electrolytic dissociation, salts in dilute aqueous solution are almost completely ionised, and Ostwald pointed out that it follows from this that the colour and absorption of dilute solutions must be due to the presence of a particular "colour-producing" ion. The absorption of dilute solutions of all salts yielding the same coloured ion should therefore be the same, whilst in more concentrated solutions the absorption would be due both to the undissociated molecules and to the ions, and would therefore be modified in character.

The fact that the different salts of a metal may show absorption spectra which differ in certain respects was observed in 1866 by Bunsen in the case of didymium, and has been established for neodymium and praseodymium, the constituents into which Bunsen's didymium has since been resolved, and for many other salts. Dilution of the solutions of these salts, however, does not invariably bring about complete identity of absorption, and a striking instance of this is afforded by the metallic nitrates, each of which shows a characteristic absorption spectrum in the ultra-violet, differing according to the metal which is present (Hartley).

In other cases, examples of which are the bromide, chloride, nitrate, and sulphate of copper (Ewan), and the metallic permanganates (Vaillant), the absorption spectra of the different salts are practically identical, and are not greatly altered by dilution, although the dissociation is thereby increased.

It is evident that the absorption produced by aqueous solutions of salts is a very complex phenomenon, the complete analysis of which has not yet been effected.[1]

93 Solutions of metallic salts are not the only liquids which exhibit this power of selective absorption. Many organic

[1] See Baly's *Spectroscopy*, 1912 edition, p. 466; also Houstoun, *Proc. Roy. Soc. Edin.*, 1911, **31**, 521–558.

liquids possess it in a high degree, and by this means complicated liquids of animal and vegetable origin can be easily distinguished when no other method is available. As an example of selective absorption in organic liquids, the spectrum reaction of blood may be cited. No. 1, Fig. 25, exhibits the two dark bands, situated between Fraunhofer's D and E, seen in oxidised blood, and due to oxyhæmoglobin. No. 2 on the same figure shows the absorption spectrum of deoxidised or venous blood, consisting of one dark band. By the action of an acid on blood, the oxyhæmoglobin is converted into hæmatin, yielding a different absorption spectrum. The hæmatin, like the oxyhæmoglobin, is capable of undergoing oxidation and reduction. The absorption bands of hæmatin are shown in Nos. 3 and 4, Fig. 25. Another interesting fact is that the

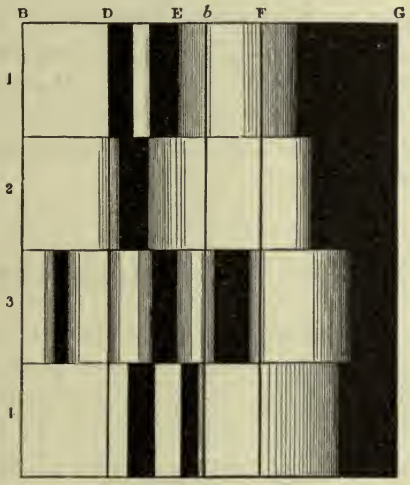


Fig. 25.

blood, when it contains very small quantities of carbon monoxide in solution, exhibits a very characteristic set of absorption bands. Carbon monoxide acts, however, as a very violent poison, and these bands are seen in the blood of animals which have been suffocated in the fumes of burning charcoal. In the same way, the peculiar compound which hæmoglobin forms with hydrocyanic acid yields a characteristic absorption spectrum. The instrument with which these absorption spectra can be observed with extremely small quantities of the liquids is a spectroscope placed in connection with a microscope. The

eyepiece contains prisms so arranged that the refracted rays pass in a straight line from the object into the eye. Such spectroscopes are termed direct-vision instruments, and are very portable and useful forms of the apparatus. This instrument, in the hands of Sorby, has proved capable of detecting $\frac{1}{1000}$ part of a grain of blood in a blood-stain.

The same observer states that wines of different vintages may be distinguished by a variation in their respective absorption spectra.[1]

Many substances which are transparent to ordinary light show very characteristic absorption bands in the ultra-violet or infra-red portions of the spectrum. Thus Abney and Festing[2] have ascertained the position of the bands and lines produced in the infra-red spectrum by many elements and groups of elements and radicals, whilst Hartley[3] has shown that the aromatic compounds are characterised by well-marked absorption bands in the ultra-violet, the position of the bands being intimately connected with the constitution of the substance. He has even been able to decide between several possible constitutional formulæ for a substance by the character of its ultra-violet absorption spectrum.[4]

COMPOSITION OF THE SOLAR ATMOSPHERE.

94 When sunlight is allowed to fall upon the slit of a spectroscope, the solar spectrum thus obtained is observed to differ essentially from the spectra which we have hitherto considered. A bright band is seen stretching from red to violet, but this band is cut up by a very large number of fine black lines. These lines are always present, and always occupy the same relative position in the solar spectrum—they are, in fact, shadows in the sunlight. They were originally noticed by Wollaston, but first carefully mapped by Fraunhofer, the principal lines being designated by him with the letters of the alphabet. Fig. 26 is a reduced facsimile of Fraunhofer's original map.

The cause of these dark solar lines was long a mystery.

[1] *Chem. News*, 1869, **20**, 295. [2] *Proc. Roy. Soc.*, 1881, **31**, 416.

[3] *Journ. Chem. Soc.*, 1885, **47**, 685; 1888, **53**, 641.

[4] See Hartley, "Relation between Absorption and Constitution of Organic Substances," Kayser, *Handbuch der Spectroscopie*, vol. ii. chap. 3 (Hirzel, Leipzig, 1905), where a detailed account of this subject is given; also Baly's *Spectroscopy*, 1912 edition.

Fraunhofer, finding that sunlight, both direct and reflected as moonlight, always gave the same lines, whereas the light of the

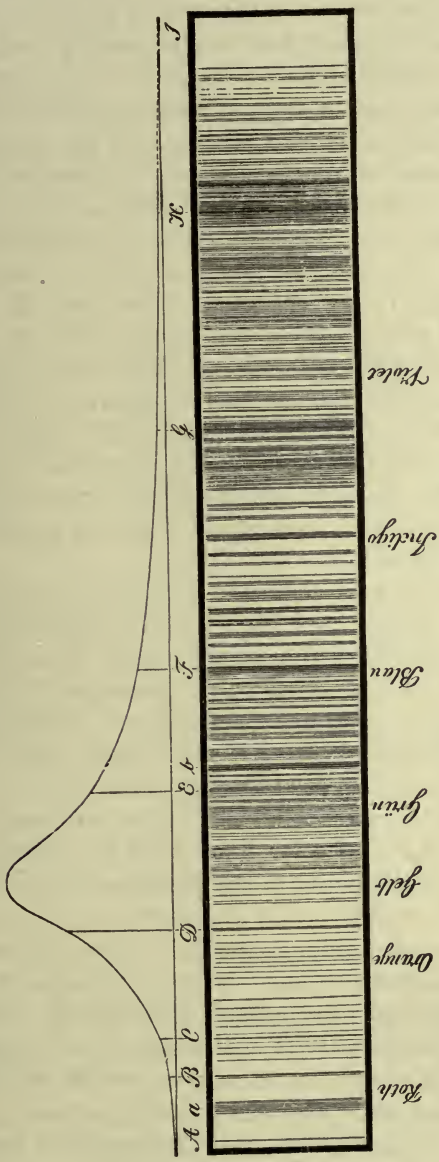


FIG. 26.

fixed stars contained different dark lines, came to the conclusion in 1814 that these dark lines were produced in the solar

atmosphere, and not by the passage of the light through the intervening space, or through our own atmosphere.

It was not until the year 1860 that the true cause of the production of these lines was first clearly proved by Kirchhoff, although the same cause had already been suggested by Stokes as a possibility. Kirchhoff was engaged in the comparison of the bright lines of certain metallic spectra with the dark lines in the sun. To his astonishment he found that *all* the bright lines of such metals as iron, calcium, and magnesium have dark representatives of the solar spectrum. Not only has each bright metal line a dark one coincident with it, but the breadth and intensity of the bright metal line are as a rule reproduced in the dark line of the solar spectrum; this may be seen by allowing a solar and a metallic spectrum to fall one below the other in the field of the telescope. Other metals, for instance, gold and antimony, exhibit no such coincidences; not a single bright line of these is found coincident with a dark solar line. It is clear, therefore, that there must be some kind of connection between the bright lines of metals of the former class and the dark solar lines. Such coincidences cannot possibly be the result of mere chance.

We have already seen that the spectrum of sodium can be reversed. By passing the light from incandescent sodium through the vapour of the metal, the bright yellow double line is changed to a dark one. If the solar atmosphere contained the vapours of sodium, of iron, of magnesium, of calcium, &c., in the state of glowing gas, and if white light from the incandescent mass beneath passed through these vapours, the effect produced would be exactly that which is in fact observed. The coincidence of the *dark* solar lines with the *bright* iron lines may therefore be attributed to the presence of iron in the sun's atmosphere.

"As this is the only assignable cause, the supposition appears to be a necessary one. These iron vapours might be contained either in the atmosphere of the sun or in that of the earth. But it is not easy to understand how our atmosphere can contain such a quantity of iron vapour as would produce the very distinct absorption-lines which we see in the solar spectrum; and this supposition is rendered still less probable by the fact that these lines do not appreciably alter when the sun approaches the horizon. It does not, on the other hand, seem at all unlikely, owing to the high temperature which we

must suppose the sun's atmosphere to possess, that such vapours should be present in it. Hence the observations of the solar spectrum appear to me to prove the presence of iron vapour in the solar atmosphere with as great a degree of certainty as we can attain in any question of physical science" (Kirchhoff).

By observing the coincidences of the dark solar lines with the bright lines of terrestrial elements we may deduce the constituents of the solar atmosphere. The elements the existence of which in the sun has now been ascertained, thanks to the labours of Kirchhoff, Ångström, Thalén, Lockyer, Kayser, Runge, and Rowland, are the following:

Elements contained in the Sun's Atmosphere.

Aluminium.	Helium.	Palladium.
Barium.	Hydrogen.	Rhodium.
Cadmium.	Iron.	Scandium.
Calcium.	Lanthanum.	Silicon.
Carbon.	Lead.	Silver.
Cerium.	Magnesium.	Sodium.
Chromium.	Manganese.	Strontium.
Cobalt.	Molybdenum.	Tin.
Columbium.	Neodymium.	Titanium.
Copper.	Nickel.	Vanadium.
Erbium.	Nitrogen (as	Yttrium.
Germanium.	cyanogen).	Zinc.
Glucinum.	Oxygen.	Zirconium.

Presence Doubtful.

Iridium.	Potassium.	Thorium.
Lithium.	Ruthenium.	Tungsten.
Osmium.	Tantalum.	Uranium.
Platinum.		

The solar corona yields a spectrum of bright lines, none of which have as yet been identified with the lines of any terrestrial spectrum.

STELLAR SPECTRA.

95 In a similar way W. Allen Miller and Huggins have succeeded in proving that various elements, including hydrogen,

sodium, calcium, magnesium, iron, occur in the atmosphere of the star Aldebaran, whilst other stars have been shown to contain other elements. The photographic mode of record was applied by Huggins to the spectra of stars, and has yielded permanent pictures of the dark lines in the stellar spectra drawn by nature herself.

From the observations of Secchi and others it appears that the stars may be divided into four main classes according to the general nature of the spectra which they present. In those of the first class, metallic vapours are not conspicuous, the spectra being characterised mainly by strong dark lines corresponding in position to the bright lines of hydrogen, as is the case in Sirius, Vega, and most white stars. In some of the stars of this class, dark lines of helium, oxygen, nitrogen, silicon, and carbon are present. The second group contains the yellow stars such as Pollux, Capella, Aldebaran, &c., the spectra of which resemble that of the sun, containing numerous dark lines due not only to hydrogen, but also to metals. The members of the third group, which comprises the red stars such as Betelgeux and α Herculis, in addition to some dark lines show fluted spectra, which have been found to be due to the presence of titanium oxide[1] in their atmospheres. Stars of the fourth type exhibit fluted spectra due to some compound of carbon in the incandescent state. Apart from the classification just given there are a few stars, such as β Lyra and γ Cassiopeiæ, which exhibit bright line spectra. Nebulæ show, as a rule, very simple spectra of bright lines, among them those of hydrogen and helium, together with others not yet identified.

The simpler a spectrum is, the simpler must be the composition of the body which yields that spectrum. Arguing upon these premisses, Lockyer concludes that the atmospheres of the whiter stars contain the fewer elements and those of smaller atomic weight, and that as the peculiar colour of the star becomes more distinct its atmosphere becomes more complicated. These results, coupled with the well-known fact that dissociation of chemical compounds uniformly takes place if the temperature is only sufficiently high, have led Lockyer to suggest that, the heat being greatest in the white stars, their simple spectra can be best explained by the existence of a temperature sufficient to dissociate the substances to which on

[1] Fowler, Monthly Notices, *Roy. Astronom. Soc.*, 1909, **69**, 508.

this earth we give the name of elementary bodies.[1] Recent research, however, makes it increasingly probable that all the lines in celestial spectra will ultimately be identified with those of terrestrial spectra.[2]

[1] See further, Roscoe's *Lectures on Spectrum Analysis* (4th edition, Macmillan, 1885); Lockyer, *Chemistry of the Sun* (Macmillan, 1887), *Inorganic Evolution as Studied by Spectrum Analysis* (Macmillan, 1900), *Proc. Roy. Soc.*, 1887, **42**, 37; 1888, **43**, 117; 1910, *A*, **84**, 426.

[2] See *Nature*, 1912, **90**, 466.

CRYSTALLOGRAPHY.

96 When a chemical substance passes from the gaseous or the liquid state into that of a solid, it generally assumes a definite geometrical form, and is said to *crystallise*.

A *crystal* is a solid body, formed in this way, and bounded by plane surfaces. As a rule, every chemical substance in the solid state possesses a distinct form in which it usually crystallises and by which it can be distinguished.

The occurrence of various mineral substances in distinct crystalline forms was noticed by the ancients, and they gave the name crystal (κρύσταλλος, ice) to one of these, viz., to quartz or rock-crystal, because they believed that this body owed its formation to the effect of cold. The Latin Geber was aware that crystals can be obtained artificially by the evaporation of a solution of a salt. He describes the production of several chemical compounds in the crystalline condition, and shows how they may be purified by recrystallisation. Many years, however, elapsed before this property of matter was regarded as anything more than an unimportant one. Libavius, it is true, asserted in the year 1597 that the nature of the saline components of a mineral water could be ascertained by an examination of the crystalline forms of the salts left on the evaporation of the water. But so imperfect were the views regarding the formation of crystals that Lemery classified them simply according to their thickness, believing that this was dependent upon the size of the ultimate particles of the acids contained in the salts. In the year 1703, Stahl pointed out that the compounds obtained by the action of acids upon sea-salt crystallised in forms different from those assumed by the corresponding compounds of potash, and hence he concluded that sea-salt contained a peculiar alkali, distinct from the common alkali potash. Guglielmini appears to have held much more

rational views than Lemery concerning the formation of crystals. In his *Dissertatio de Salibus*, published in 1707, he asserts that the smallest particles possess definite crystalline forms, and that the differences in form which we observe between the crystals of alum, nitre, and sea-salt are caused by similar differences existing between the forms of the smallest particles.

It is, however, to Haüy (1743—1822), that we are indebted for the foundations of the science of crystallography. Haüy was the first to point out the fact that every crystalline substance possesses certain definite and characteristic forms in which it crystallises, and that all these different forms can be derived from one fundamental form which can be ascertained by measurement of the angles of the crystal. Upon this principle he founded in 1801 his celebrated system of the classification of minerals.

General Characteristics of Crystals.—A crystal of any substance is characterised, in the first place, by its special geometrical form, and, in the second place, by its physical properties, both of which we must suppose to be due to the special mode of arrangement of the particles of which the crystal is built up. In an amorphous, or non-crystalline, substance the physical properties are as a rule the same in every direction throughout its mass, whilst in a crystalline substance this cannot be the case for all of them. Thus, for example, under ordinary conditions light travels through a piece of glass at the same rate in whatever direction it may happen to pass, whilst in a crystal of quartz or calcspar the rate is different in different directions. The physical properties are even more characteristic of a crystalline substance than the geometrical form which it assumes, and can be recognised in fragments of the substance in which the characteristic crystalline form may be quite unrecognisable.

Parts of a Crystal; Faces, Edges, Corners, and Zones.—A typical crystal of quartz or rock-crystal, SiO_2, is shown in Fig. 27. The plane surfaces by which the crystal is bounded are termed *faces*. The straight lines formed by the intersection of two contiguous faces are the *edges*. Solid angles or *corners* are made by the intersection of three or more faces at a point, and are sometimes also termed summits. In the given crystal there are evidently two kinds of corners, namely, those in which four faces meet, and those in which six faces meet.

A remarkable feature of the development of crystals is that

no matter how great the number of faces, they can be divided into a relatively small number of *zones, i.e.* sets of faces intersecting in parallel edges; *e.g.* the six vertical faces in Fig. 27 lie in a zone with vertical edges. There are three other obvious zones, each of which includes two vertical faces and four pyramid faces, the edges of intersection being horizontal. The eighteen faces, then, on the crystal lie in four zones. This predisposition of a relatively large number of faces to lie in a zone greatly simplifies the measurement of a crystal. A line drawn through the centre of the crystal parallel to a zone edge is termed the zone axis.

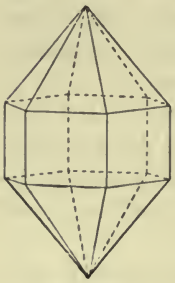


Fig. 27.

Distortion of Crystals.—Crystals of alum are bounded by eight faces inclined at the same angles as the regular octahedron of Fig. 28, but the shape of the crystal rarely obtains such an ideal development; more often it approximates to that of Fig. 29. A comparison of the two figures will show that the deposition of parallel layers of material on the large pair of faces of the latter figure would transform it into the ideal shape. This deposition does not alter the angles between the faces. Such a departure of the shape from that of the ideal form is termed *distortion,* and is due to the more favoured position of some of the faces of the

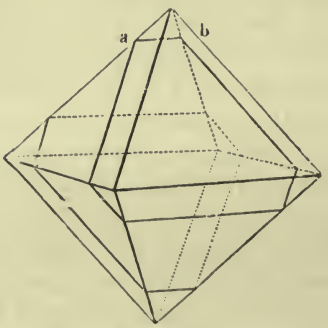


Fig. 28.

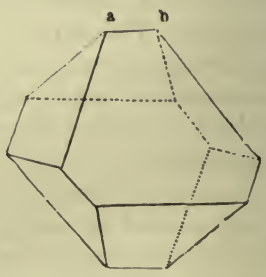


Fig. 29.

crystal in the solution during growth. If a small distorted crystal be carefully turned over from time to time so as to rest on different faces during growth, it will gradually assume the ideal form.

97 *Measurement of Crystals.*—The instrument now used for

this purpose is the reflecting goniometer invented by Wollaston in the year 1809, a modern form of which is shown in Fig. 30. Suppose the crystal to be measured is the quartz crystal of Fig. 27. By means of a little wax it is placed in a vertical position with its pointed end on a small pin which fits into a corresponding hole at the upper end of the central axis of the instrument, and is clamped tight by means of the top small

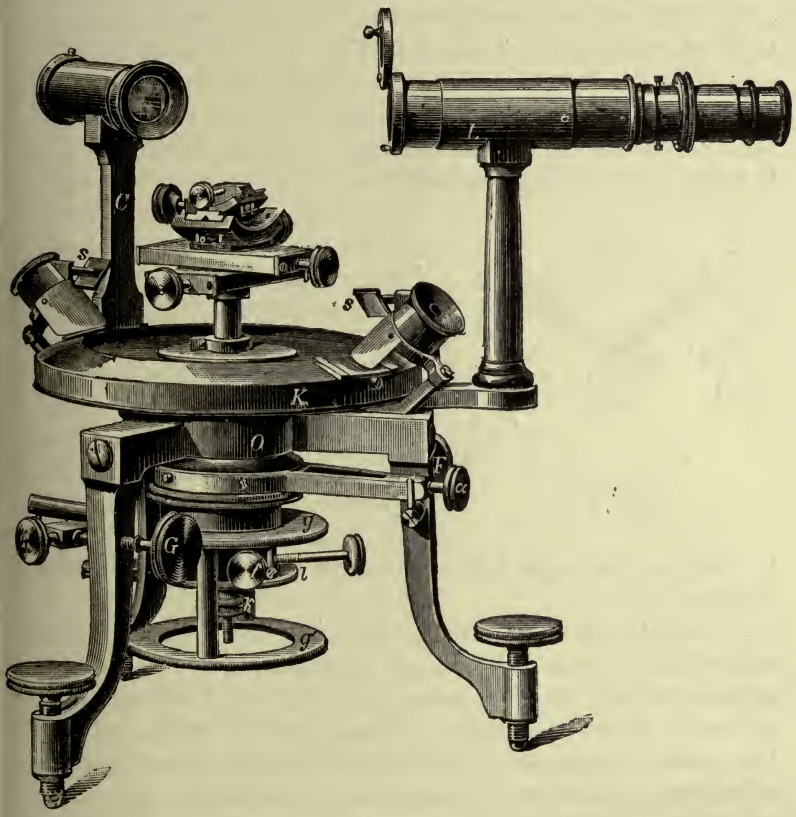


FIG. 30.

screw. The other screws, seen at the upper end of the axis, are for centring and tilting the crystal so as to bring the edges truly vertical. The remaining parts of the instrument are:—the divided circle, *K* (provided with verniers *ss* for taking the readings), which is clamped to the central axis, the whole being rotatable by means of the milled ring, *g'*, at the bottom of the instrument. Light from an incandescent burner is sent through

a slit at the end of the collimator C and falls on the crystal. The telescope L, is fixed at a convenient angle to C (say a little over a right angle), and the crystal is rotated till the image of the slit, reflected from a face, comes on to the cross-wires in the telescope. When the reading has been taken, the crystal is rotated and successive readings are noted for the various faces till a full rotation of 360° has been carried out. The differences between successive readings will be found to be 60° 0′. The position of one of the faces while a reading is being taken, as viewed from the top of the instrument, is shown in Fig. 31. It is seen that the normal to the face, namely N, bisects the angle between collimator and telescope, and in order to bring the next face into the same position it is necessary to rotate the crystal 60°. It follows that the angle actually measured is the outside angle, or the angle between the normals to the two faces, and not the internal angle, which in this case would be 120°. These outside measured angles are the ones usually employed in modern writings, a fact which should be borne in mind. After a complete zone has been measured, the crystal is removed, and adjusted on the wax with another set of faces vertical, and the process is repeated till all the faces have been measured.

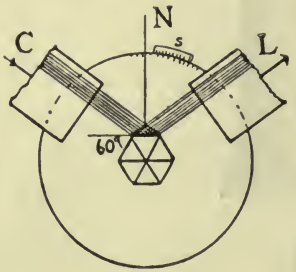


FIG. 31.

As will be shown in the next section, the angles between edges have great theoretical significance. The simple goniometer just described records only the angles between pairs of faces ("interfacial angles"); from them the angles between the various edges can be obtained by simple trigonometrical calculation. In recent years, however, goniometers have been constructed, provided with two, or even three, divided circles, which admit of a direct measurement of the angles between edges as well as the interfacial angles.

98 *The Fundamental Law of Geometrical Crystallography.*— The difference in appearance between two crystals of the same substance, even when they are of the same crop, may be due to another factor besides distortion, viz., a difference in the number of faces: not only may some faces be suppressed, but in addition to the usual faces a crystal may occasionally exhibit an alto-

gether new set of faces. It is therefore not surprising that the view was formerly held that each individual crystal has its own shape; and it was only after crystals began to be measured that a simple mathematical relationship was discovered between the various shapes. The nature of this relationship will now be discussed.

Crystals of common salt are generally cubes with small triangular facets on the corners (Fig. 32); the latter on measurement are found to be inclined to one another at the same angles as the faces of a regular octahedron. Through the centre, *O*, of the crystal let three axes, *OX*, *OY*, and *OZ*, be drawn parallel to the three cube edges. Now imagine the facet, *p*, extended in space till it meets the axes in the points *A*, *B*, *C*;

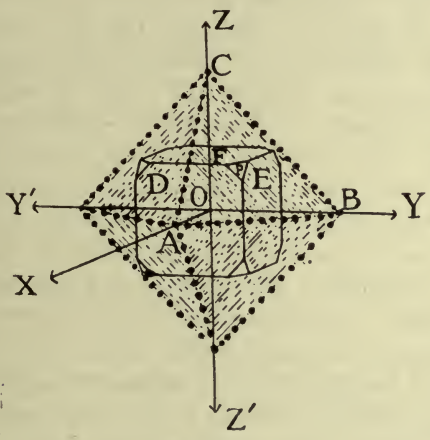


FIG. 32.

the lengths *OA*, *OB*, *OC*, are the *intercepts* of the face *p* on the axes *OX*, *OY*, and *OZ*. The actual lengths *OA*, *OB*, *OC*, obviously depend on the perpendicular distance of the face *p* from the point *O* at the centre of the crystal, and as a crystal grows they they will all increase in magnitude. Since, however, during growth the face *p* remains parallel to itself, the ratios of the three intercepts, viz. *OA* : *OB* : *OC* remain constant. These ratios, generally denoted by $a : b : c$, are termed the *parametral ratios* (or *axial ratios*) of the crystal, the face *p* the *parametral plane*, and the three axes, *OX*, *OY*, *OZ*, the *crystallographic axes*.

It is thus found that the intercepts of any other face of the crystal can be expressed by the ratios $ma : nb : oc$, where m, n, and o are rational whole numbers (or in some cases infinity).

This relation is known as the *Law of Rational Intercepts* and has been verified in every case investigated.

In the instance just considered (viz., salt) $a=b=c$, but in other substances they may be unequal.

If the other three front corner facets be extended in a precisely similar manner it is found that their intercepts have exactly the same ratios $a:b:c$, but when allowance is made for the fact that they intercept certain of the axes towards their negative ends (X', Y', Z'), the intercept ratios of the three facets are seen to be $a:-b:c$, $a:-b:-c$, and $a:b:-c$. The extensions of the four corresponding facets at the back of the crystal are not put into the figure; they have this in common, that they meet the negative end of the axis OX.

The intercepts of the three faces D, E, F, must now be considered. To take D. The axes OY and OZ were drawn parallel to the edges between DF and DE respectively, *i.e.*, to two directions lying in the plane D. Since, however, they were drawn through the centre of the crystal which lies at the back of D, it is easy to see that however far the plane D be extended, it will never meet the axes OY and OZ. Its intercepts, then, on these axes are of infinite length. Its intercept on the axis OX is finite and the ratios of the intercepts of the face D are $1a:\infty b:\infty c$. Similarly, the intercepts of the faces E and F are in the ratios $\infty a:1b:\infty c$, and $\infty a:\infty b:1c$.

The parametral or axial ratios, $a:b:c$, are calculated by trigonometrical methods from the measured angles. Now, *with the exception of crystals belonging to the cubic system* (cf. p. 193), the angles of no two substances are alike, and it follows that *the parametral ratios have different numerical values for each separate substance.*

Millerian Indices.—It is convenient to replace the system of intercepts by one of "indices," the use of which was introduced by W. H. Miller. The indices of any face are derived from the intercepts by a simple algebraic transformation. For example, the intercepts $1a:\infty b:\infty c$ may be written in the form $\frac{a}{1}:\frac{b}{0}:\frac{c}{0}$ (for $\frac{b}{0}=\infty b$, etc.); the denominators 1, 0, 0, enclosed in a bracket, thus (100), are the *indices* of the face D (Fig. 32). Similarly, we obtain E-(010) and F-(001). The intercepts of p, viz., $1a:1b:1c$, become $\frac{a}{1}:\frac{b}{1}:\frac{c}{1}$, hence the indices are (111). It will be noted that

when a face is parallel to any axis its intercept is ∞, and the corresponding index is 0. In the case of a negative intercept the minus sign is placed over the corresponding index. The indices of all the faces are shown in Fig. 33. The indices of a face constitute its *symbol*, and the symbol determines unambiguously the direction of the face on the crystal: thus (213) means that the face has intercepts in the ratios $\frac{a}{2}:\frac{b}{1}:\frac{c}{3}$, where a, b, and c are the parametral lengths of the crystal in question.

Form.—This term, in addition to its ordinary meaning "shape," is employed in a very special sense in crystallography, the precise nature of which will now be explained. As has already been stated, the physical properties of a crystal vary with the direction; *e.g.*, the cohesion of a crystal is less in certain directions than in others, and the difference is often so pronounced that on subjecting the crystal to fracture it breaks quite easily along certain planes so as to afford brilliantly reflecting *cleavage* surfaces. A crystal of common salt may be easily cleaved into thin flakes parallel to the three faces *D*, *E*, *F*, whilst attempts to break the crystal in other directions, say along the octahedral facets, merely lead to very irregular fractures. The perfection of the cleavage is exactly the same for the three pairs of cube faces, and the same absolute similarity is found to extend to every physical property that has been investigated. Again, the four octahedral planes are similar in every respect. Such a *group of physically similar faces* is known as a *form*; the six cube faces constitute the cube form, the eight octahedron faces the octahedron form. When several forms are developed on the same crystal it is said to exhibit a combination of forms.

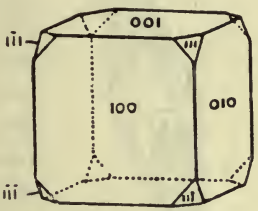


FIG. 33.

It will be noted that the indices of the faces constituting the cube and octahedron forms are permutations of the numbers (100) and (111) respectively, including plus and negative signs. This regularity has really resulted from a wise choice of the three crystallographic axes and parametral plane, and is very desirable, since crystallographic descriptions are much simplified thereby. A complete form is often denoted by enclosing the

indices of one of the faces in broken brackets, *e.g.*, {111} designates the whole octahedral form.

SYMMETRY OF CRYSTALS.

99 Symmetry is a property of frequent occurrence in natural objects: the higher forms of life are characterised externally by bi-lateral symmetry—the two halves bearing a very obvious relationship to each other. But it is in the crystal kingdom that symmetry reaches its highest form, for, as a rule, not only does the external form exhibit symmetry of a high order, but a study of the physical properties discloses the fact that the internal structure is also endowed with symmetry; and the conclusion may be safely drawn that the symmetry of external form is a manifestation of a unique, and regular, molecular arrangement. The form of a crystal often appears to be of a most complicated character, but when viewed in the light of symmetry it never fails to acquire the utmost simplicity. Symmetry again provides a sure basis of classification with regard to both the external form and the physical properties. There are three kinds or "elements" of symmetry to be considered: plane, axis, and centre of symmetry.

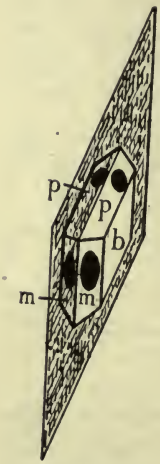


Fig. 34.

Plane of Symmetry.—Any plane which divides a crystal into parts which are geometrically similar, so that one part bears the same relation to the other as it would to its image in a plane mirror placed in the same position as the dividing plane, is called a *plane of symmetry.* Thus in Fig. 34, representing a crystal of gypsum, $CaSO_4,2H_2O$, the plane of symmetry which bisects the crystal parallel to the face *b* is indicated by shading, and it is seen that the two faces, *mm*, occupy mirror image positions with respect to that plane: the same holds for the other faces, *pp* and *bb*, as well as all the edges on the crystal. Such a crystal is said to have a plane of symmetry parallel to *b*. The symmetrical character of the crystal about this plane in regard to physical properties can be proved by means of a simple experiment. On pressing the point of a red-hot needle against the faces, dehydration

commences and as a result of a difference of the conductivity for heat in different directions, elliptical, and not circular, opaque rings of plaster of Paris are formed, which show up very well against the clear, unaffected parts of the crystal. Now on examination it is found that not only are the ellipses on the faces *mm* similar in curvature but also in orientation with respect to the plane of symmetry. Further proof of the existence of the same plane of symmetry in the physical sense is afforded by the relative orientation and curvature of the ellipses on the faces *pp*.

Axes of Symmetry.—If the crystal of potassium periodate, KIO_4, (Fig. 35) be rotated about the vertical axis *Z*, through an

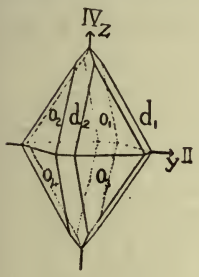


Fig. 35.

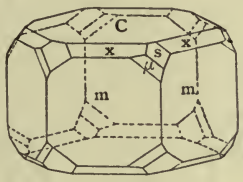


Fig. 36.

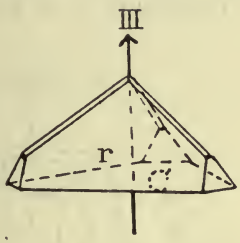


Fig. 37.

angle of 90°, the face o_1 will come into the position of o_2, o_3 into o_4, d_1 into d_2, etc. Further rotations of 90° serve to bring every part of the figure again into coincidence. Such an axis of rotation is termed an *axis of symmetry*, and as complete coincidence occurs four times during a complete rotation of 360°, the axis is designated *four-fold* or *tetragonal*. On the other hand, when rotated about the axis *Y* the rotation necessary to bring each face into the position formerly occupied by a similar face is 180°; so that this direction is termed a *two-fold* or *digonal axis of symmetry*. The crystal of apatite (Fig. 36) has a vertical axis of *six-fold* or *hexagonal symmetry* emerging through the centre of the top face, whilst in the crystal of sodium periodate, $NaIO_4,3H_2O$ (Fig. 37), the vertical direction is one of *three-fold* or *trigonal symmetry*.

Alternating Axes of Symmetry.—Crystals of urea, $CO(NH_2)_2$, Fig. 38, appear at first sight to have a vertical axis of two-fold symmetry. But consider the face p_1: if it be rotated 90° about the vertical axis and subsequently reflected across the horizontal, shaded plane, it comes into the position of p_2, and the same

coincidence holds for the crystal as a whole. An axis of symmetry of this peculiar character is termed an *alternating axis of four-fold symmetry.* An *alternating axis of six-fold symmetry* is exhibited by the mineral calcite, $CaCO_3$, a rare form of which is shown in Fig. 39. The crystal appears to have a vertical six-fold axis of ordinary symmetry. If, however, the crystal be immersed in a dilute solution of hydrochloric acid for a few seconds, then washed free from the acid and viewed with a lens, etched figures are seen. These figures are due to the fact that the solubility of a crystal is different along different directions, but the same along similar directions; the etched figures have, moreover, a similar form and a symmetrical orientation on similar faces. Although the form of the figures is the same on all the vertical faces, yet the orientation is only

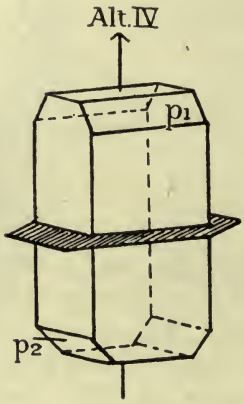


Fig. 38.

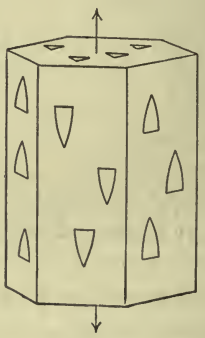


Fig. 39.

similar on alternate faces; if the etched figures be rotated 60° about the vertical axis and then inverted by reflection across a horizontal plane, coincidence becomes complete: the vertical axis is really an alternating six-fold axis of symmetry. Reliance on the geometrical form often suggests too high a symmetry; the method of exploring crystal structures by means of etched figures is most valuable in unmasking the true symmetry.

Centre of Symmetry.—When the physical and geometrical properties of a crystal are the same along both directions of each and every line in the crystal, the crystal is said to possess a *centre of symmetry.* The presence of a centre of symmetry is shown geometrically when each and every face is accom-

panied by a similar parallel face; *e.g.*, the crystal of copper sulphate, $CuSO_4,5H_2O$, shown in Fig. 40.

It must be remarked that a crystal need not necessarily possess any of the above elements of symmetry. Such a crystal is completely asymmetric in the fullest sense. Calcium thiosulphate, $CaS_2O_3,6H_2O$, is an example (Fig. 41); it will be noticed that several of the faces have no corresponding parallel faces at the back.

100. *The Thirty-two Classes of Crystals.*—The various elements of symmetry which have been described are the only kinds exhibited by crystals, and it is easy to show that no other elements of symmetry are possible in a body obeying the law of rational intercepts: *e.g.*, a five- (seven- eight-, etc.) fold axis

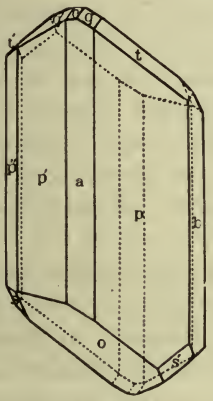


Fig. 40.

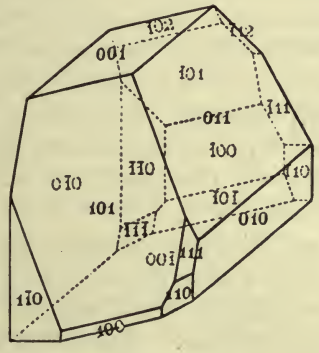


Fig. 41.

of symmetry would lead to the development of faces with irrational intercepts. Now most of the crystals used as illustrations in the preceding section possess more symmetry than was actually mentioned; most of those containing axes of symmetry also exhibit one or more planes of symmetry, and also a centre of symmetry. The following question then arises: "What combinations of the various elements of symmetry are possible in a crystal obeying the law of rational intercepts?" This mathematical problem has been completely solved, and the number of classes, or combinations of symmetry, is thirty-one; adding to this the asymmetric class, the number thirty-two is finally obtained. Of the thirty-two classes theoretically possible, representatives of at least thirty have been recognised amongst the substances already measured.

The number of substances crystallising in each class is very disproportionate; one or two of the classes are hitherto only represented by a single substance, whilst others include many thousands. A reference-list of the thirty-two classes is given on page 201.

The word *form* has already been defined as the collection of faces having similar physical properties; it must be added that they must also be similar in the geometrical sense. Now, even in the same crystal, the number of faces constituting the various forms is not the same. In the crystal of sodium periodate (Fig. 37, p. 183) the vertical three-fold axis is the only element of symmetry, and it is perpendicular to the base *C*. On rotating the crystal through successive angles of 120° about this axis, the face *C* never occupies any other direction in space; but a face like *r* on such rotation gives rise to two other similar faces. The form *r* therefore consists of three faces, whilst the form *C* is represented by one face. It may be stated that the number of faces constituting the form depends on the relative position of the faces with regard to the elements of symmetry. In those classes where there are several elements of symmetry, the possibility of variation is naturally greatly increased.

101. *The Seven Systems.*—In addition to the division into the thirty-two classes according to symmetry there has long been in use another classification of a coarser character, viz., into the seven "systems." The latter classification was already in use before the question as to the possible number of classes of symmetry had been exhaustively studied. When the crystallographic axes and parametral face have been chosen so that the various faces of a form obtain similar intercepts, or in other words similar indices, it is found that the relative inclination of the axes and their parametral lengths correspond to one of the following seven cases, or *systems*, and the crystal is reckoned as belonging to that system:

Crystallographic Axes and Parameters.	System.
1. Three axes unequally inclined; with unequal parameters	Triclinic, Anorthic or Asymmetric.
2. Three axes, one perpendicular to the other two; with unequal parameters	Monoclinic or Monosymmetric.
3. Three axes, all at right angles; with unequal parameters	Rhombic or Orthorhombic.
4. Three axes, all at right angles; with two out of the three parameters equal	Tetragonal or Quadratic.
5. Three axes, mutually inclined at equal angles (not a right angle); with all three parameters equal	Rhombohedral or Trigonal.

Crystallographic Axes and Parameters.	System.
6. Four axes, one perpendicular to the remaining three, which are mutually inclined at 60°; with parameters of the last three axes equal	Hexagonal.
7. Three axes, mutually perpendicular; with all three parameters equal	Cubic, Tesseral or Regular.

In this way the thirty-two classes may be distributed into seven systems. The classes which fall within one and the same system bear a pronounced family likeness: the class with highest symmetry contains all the elements of symmetry exhibited by the other classes in the same system and, except in the trigonal system, is the most common class. In the following short description of the various systems, the most common class will be the one selected to represent each system; a few of the remaining, less symmetrical, classes which are of chemical interest will be discussed subsequently.

It can be proved that the direction (1) of an axis of symmetry or (2) of a line perpendicular to a plane of symmetry, is a possible edge, *i.e.*, an edge between faces having rational intercepts; and it is therefore permissible to use such directions as crystallographic axes although they may not be actually developed as edges. It should be noted that axes of symmetry and crystallographic axes are not interconvertible terms; the latter are as a rule chosen parallel to the former, but this is not always so. Moreover, there is often a greater number of axes of symmetry than of crystallographic axes, the number of the latter being only three, with the single exception of the hexagonal system, which has four.

1. The Triclinic, Anorthic, or Asymmetric System.

102 The three crystallographic axes, *OX*, *OY*, *OZ*, may be selected parallel to any three edges on the crystal, and are in any case inclined at different angles, usually denoted by α, β, and γ. The parametral lengths of these three axes are unequal.

Example.—Potassium dichromate, $K_2Cr_2O_7$. (Fig. 42.)

$a:b:c = 1{\cdot}0116:1:1{\cdot}8146$; $\alpha = 98°\ 0'$, $\beta = 96°\ 13'$, $\gamma = 90°\ 51'$.

Symmetry: A centre of symmetry; each form therefore consists of a pair of parallel faces.

The edges selected for the directions of the three crystallo-

graphic axes, OX, OY, and OZ, are those between the faces B and C, C and A, A and B respectively, from which it follows that the faces A, B, C will have the indices (100), (010), (001) respectively. The parametral face chosen is p, and since it cuts the axis OZ at its negative end, the indices of p must be $(11\bar{1})$. The ratios

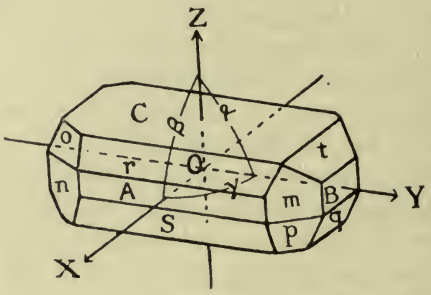


Fig. 42.

of the parameters $a:b:c$, as also the angles α, β, and γ, are calculated from the angles which these four faces make with each other. The remaining faces are then found to have the following indices: $s-(10\bar{1})$, $r-(101)$, $m-(110)$, $n-(1\bar{1}0)$, $q-(01\bar{1})$, $t-(012)$, $o-(1\bar{1}1)$.

2. The Monoclinic or Monosymmetric System.

103 One of the crystallographic axes, namely OY, is taken parallel to the only edge on the crystal which is found to be

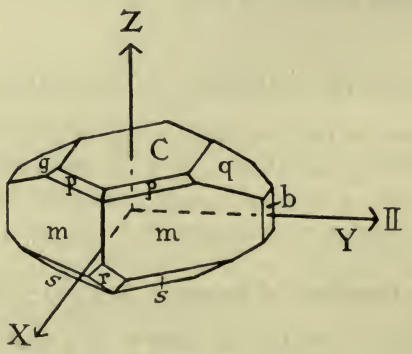


Fig. 43.

perpendicular to two other edges, and the latter are chosen for the directions of the two crystallographic axes, OX and OZ.

The latter axes are not inclined at 90°, but at some other angle, β.

Example.—Rubidium magnesium sulphate,

$$Rb_2Mg(SO_4)_2,6H_2O \text{ (Fig. 43).}$$

$$a:b:c=0{\cdot}7400:1:0{\cdot}4975\ ;\ \beta=105°\ 59'.$$

Symmetry (Class 5).—One plane of symmetry containing the axes *OX*, *OZ*, perpendicular to which is a two-fold axis of symmetry (the axis *OY*); also a centre of symmetry.

The axis *OX* is parallel to the edge *cq*, *OZ* to *mm*. The axis *OY* is a possible edge, since it is parallel to the two-fold axis of symmetry; it is the edge in which *c* and *r* would intersect. The parametral plane is $p-(111)$, the remaining forms being $m-\{110\}$, $s-\{11\bar{1}\}$, and $q-\{011\}$, each consisting of four faces; and $c-\{001\}$, $b-\{010\}$ and $r-\{20\bar{1}\}$, each consisting of two faces. There is an imperfect cleavage parallel to the last-mentioned face.

Another example of a monoclinic crystal is gypsum (Fig. 34, p. 182).

3. The Rhombic or Orthorhombic System.

104 The three crystallographic axes, *OX*, *OY*, and *OZ*, are taken parallel to a particular set of edges (or possible edges) mutually perpendicular to one another. A face which is

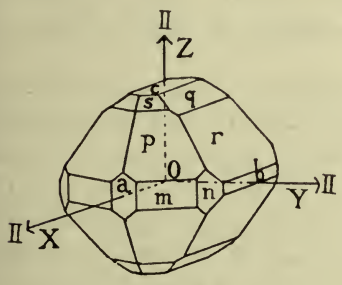


Fig. 44.

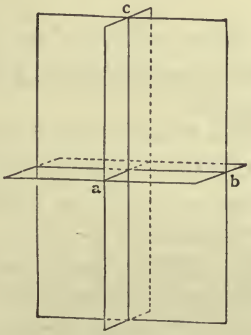


Fig. 45.

inclined to all these directions is selected as parametral plane, and gives three unequal parameters.

Example.—Potassium sulphate, K_2SO_4 (Fig. 44).

$$a:b:c=0{\cdot}5727:1:0{\cdot}7418.$$

Symmetry (Class 8).—Three planes of symmetry at right angles to one another (Fig. 45), intersecting in three two-fold axes of symmetry; also a centre of symmetry.

The crystallographic axes, OX, OZ, are taken parallel to the edges cq and am respectively. The axis OY is not developed as an actual edge, but this direction, as well as those of OX and OZ, is one of two-fold symmetry. The parametral plane is p and has therefore the indices (111). The forms $a-\{100\}$, $b-\{010\}$, and $c-\{001\}$, which are parallel to two of the axes, consist of a pair of parallel faces; forms like $m-\{110\}$, $n-\{130\}$, $q-\{011\}$, and $r-\{021\}$, which are parallel to one axis and intersect the other two, consist of four faces; finally, forms like $p-\{111\}$, and $s-\{112\}$, which intersect all three axes, consist of eight faces.

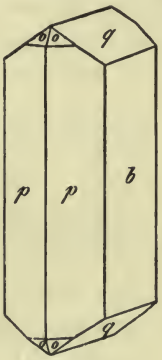


Fig. 46.

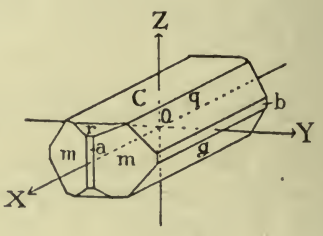


Fig. 47.

Other examples are aragonite, $CaCO_3$ (Fig. 46), and potassium perchlorate, $KClO_4$, a crystal of which is shown in Fig. 47.

The forms in the first mentioned are:—the parametral plane $o-\{111\}$, $b-\{010\}$, $p-\{110\}$ and $q-\{011\}$; and the parametral ratios are $a:b:c = 0{\cdot}623:1:0{\cdot}721$. In potassium perchlorate the forms are: $c-\{001\}$, $a-\{100\}$, $b-\{010\}$, $q-\{011\}$, $m-\{110\}$ and $r-\{102\}$. In this crystal there is no face intersecting all three axes, so recourse must be had to two parametral faces, viz., m, which decides the ratio $a:b$, and q, from which the ratio $b:c$ is calculated; $a:b:c = 0{\cdot}7815:1:1{\cdot}2805$.

4. The Tetragonal or Quadratic System.

105 The crystallographic axes, OX, OY, and OZ, are mutually perpendicular, OZ being taken parallel to the unique axis of

four-fold symmetry (or of the alternating axis of four-fold symmetry). The parametral lengths of the axes *OX* and *OY* are equal, but have a different value from that of the axis *OZ*.

Example:—Zircon, $ZrSiO_4$ (Fig. 48).

$$a = b;\ a:c = 1:0{\cdot}640.$$

Symmetry (Class 15).—One vertical four-fold axis which is perpendicular to four two-fold axes intersecting at angles of 45°. These five axes of symmetry are respectively perpendicular to

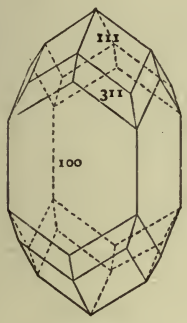


Fig. 48.

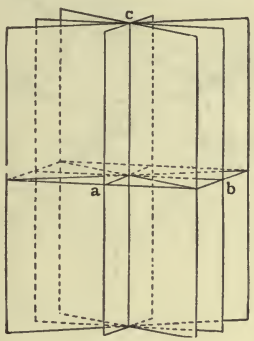


Fig. 49.

the horizontal and the four vertical planes of symmetry shown in Fig. 49.

In Fig. 48, the parametral plane is (111), which is seen to consist of eight faces. The form {100} consists of four faces, and the form {311} consists of sixteen faces.

5. The Rhombohedral or Trigonal System.

106 The most characteristic form of this system is the rhombohedron (Fig. 50), and the three crystallographic axes, *OX*, *OY*, and *OZ*, are drawn parallel to the three edges of this form. The parametral lengths are equal. The angles between the three axes, *OX*, *OY*, and *OZ*, are equal, but not right angles; these angles are denoted by α, and are calculated from the measured angles between the faces of the rhombohedron.

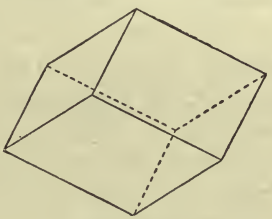


Fig. 50.

Example:—Sodium nitrate, $NaNO_3$; $\alpha = 102° 47'$. Form, the simple rhombohedron (Fig. 51).

Symmetry (Class 21).—Three vertical planes of symmetry (Fig. 52), perpendicular to each of which there is a two-fold axis of symmetry, emerging at the middle point of each of the zig-zag edges (Fig. 51), and further a vertical axis of alternating six-fold symmetry. It will be noted that none of the crystal-

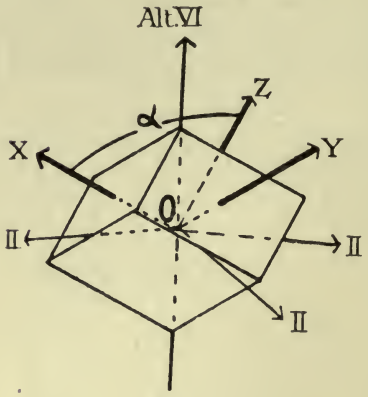


Fig. 51.

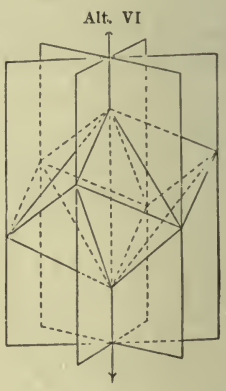


Fig. 52.

lographic axes is chosen either parallel to an axis of symmetry, or perpendicular to a plane of symmetry. Although somewhat arbitrary, it is only by means of this choice that similar faces acquire similar intercepts and indices.

Other examples are the minerals of the calcite group.

6. The Hexagonal System.

107 Here, again, the choice of crystallographic axes is peculiar, since it is found advisable to select no fewer than four. The disposition of the three axes *X*, *Y*, *Z*, intersecting at angles of 120°, and of the fourth axis *W*, which is perpendicular thereto, is shown in Fig. 53. The parameters a_1, a_2, a_3 of the axes *X*, *Y*, *Z* are equal, but the parameter *c* of the fourth axis has a different value. The parametral ratio $a:c$ is calculated from the angles between the faces shown on the figure.

Example :—Beryl (emerald), $a:c = 1:0{\cdot}4989$ (Fig. 54).

Symmetry (Class 27).—A vertical axis of six-fold symmetry and six two-fold axes of symmetry, intersecting at angles of 30° in the horizontal plane; each being respectively perpendicular

to the single horizontal and the six vertical planes of symmetry shown in Fig. 55; also a centre of symmetry.

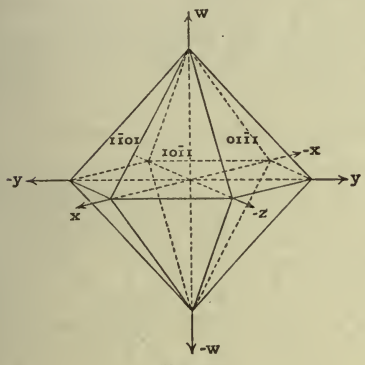


Fig. 53.

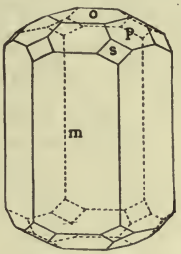


Fig. 54.

Since there are four crystallographic axes, each face has four intercepts.

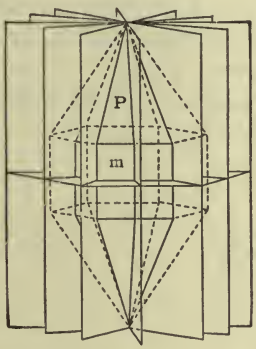


Fig. 55.

The forms in Fig. 54 are $m-\{10\bar{1}0\}$, $p-\{01\bar{1}1\}$, $s-\{11\bar{2}1\}$, and $c-\{0001\}$.

7. The Cubic, Tesseral, or Regular System.

108 Crystals of this system are referable to three mutually perpendicular crystallographic axes, with equal parameters, *i.e.*, $a=b=c$.

Examples:—Fluorspar, CaF_2; cubes with octahedral facets (Fig. 33, p. 181). Senarmontite, Sb_2O_3; regular octahedra (Fig. 32, p. 179). Garnet: Rhombic dodecahedra (Fig. 59).

Symmetry (Class 32).—The symmetry is the highest possible in all crystals and is identical with that of a cube, viz., four three-fold axes emerging through the corners, *i.e.*, perpendicular to the octahedron faces; three four-fold axes parallel to the cube edges, *i.e.*, perpendicular to the cube faces; six two-fold

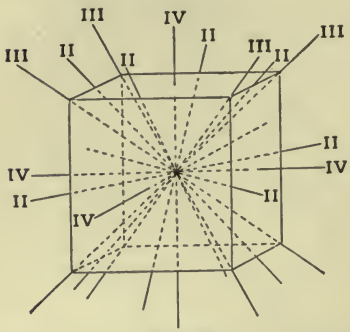


Fig. 56.

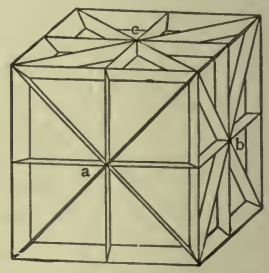


Fig. 57.

axes emerging at the mid-point of the cube edges, *i.e.*, perpendicular to the dodecahedral faces (Fig. 56). Further, three planes of symmetry parallel to the cube faces, and six diagonal planes of symmetry parallel to the dodecahedral faces (Fig. 57); also a centre of symmetry.

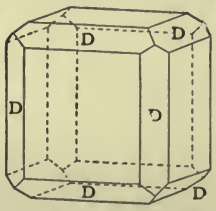


Fig. 58.

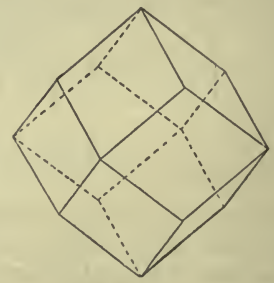


Fig. 59.

The relationship of the rhombic dodecahedron to the cube will become clear from an inspection of Figs. 58 and 59. In the first figure the dodecahedral faces are seen to truncate the twelve edges of the cube. If the twelve facets be extended in space, so as to eliminate the cube faces, they ultimately yield the simple rhombic dodecahedron of Fig. 59.

ENANTIOMORPHISM.

109 Many natural objects are not identical with their mirror images; the reflection of a right hand in a plane mirror appears to be a left hand; so that although the two hands are certainly similar, the one is easily distinguishable from the other. Bodies which can exist in two non-superposable forms which are the mirror images of each other are termed enantiomorphous. The study of geometry has led to the recognition that only those bodies can exist in enantiomorphous forms which are devoid of the following three elements of symmetry: plane, centre, and alternating axis of symmetry. The only elements of symmetry

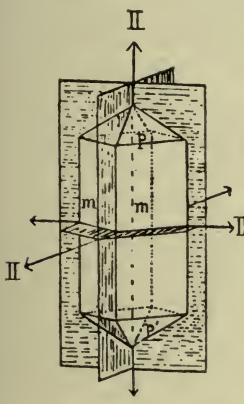


FIG. 60.

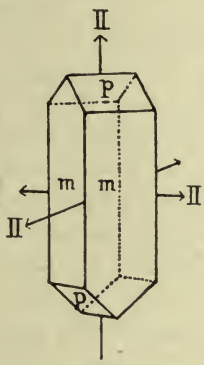


FIG. 61.

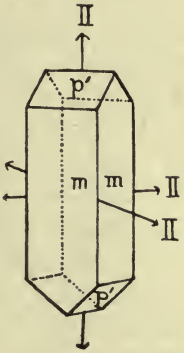


FIG. 62.

compatible with enantiomorphism are the ordinary axes of symmetry. These conditions are satisfied by eleven out of the thirty-two classes of symmetry, and examples of enantiomorphism have been discovered in crystals belonging to all these classes.

Geometrical Evidence of Enantiomorphism in Crystals.—The more important faces on crystals of magnesium sulphate, $MgSO_4,7H_2O$, are shown in Fig. 60. The crystals are orthorhombic with $a:b:c=0{\cdot}9901:1:0{\cdot}5709$, and appear to have three planes of symmetry (shaded), and three two-fold axes of symmetry as indicated. The development of the crystals, however, is sometimes of a less symmetrical character, and two kinds of crystals may be distinguished (Figs. 61 and 62). Of

the eight terminal faces in Fig. 60, only half are developed on the first crystal, the remaining half on the other crystal. The effect of this "*hemihedral*" development of the terminal faces is to indicate the absence of the three planes of symmetry; nor is there a centre of symmetry, for the faces no longer all appear in parallel pairs. The crystals still possess the three two-fold axes of symmetry, and are enantiomorphous, one being the non-superposable mirror image of the other. It may be noted that the enantiomorphism is outwardly indicated on the crystals by the p faces; each set of four p faces constitutes a form, the two forms being symbolised by $p-\{111\}$ and $p'-\{1\bar{1}1\}$ respectively. When both these forms are developed, Fig. 60 is obtained, and the crystal appears to have both planes and a centre of symmetry. The form $m-\{110\}$ consists of four faces on all the three crystals and does not afford any clue to the class of

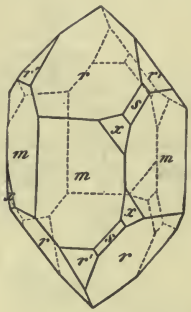


Fig. 63.

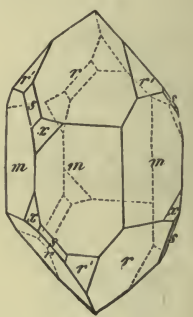


Fig. 64.

symmetry. In fact, only faces like p, which consist of half the usual number of faces, really unmask the true symmetry and exhibit geometrical enantiomorphism. In certain classes of the cubic and tetragonal systems a form may consist of only a *quarter* of the usual number of faces, and on this account is termed *tetartohedral*.

The first known example of enantiomorphism was quartz. The usual development of this mineral is that already shown in Fig. 27, p. 176, which appears to have a centre, as well as several planes, of symmetry; but etched figures prove the absence of all these elements of symmetry. Moreover, the enantiomorphism is sometimes demonstrated by the appearance of hemihedral facets, labelled x on Figs. 63 and 64, which distinguish the two kinds of crystal; the two crystals are called right- and left-handed respectively, or dextro- and laevo-crystals.

110 *Optical Activity or Rotatory Polarisation.*—The enantiomorphous development of a crystal is due to a corresponding enantiomorphism of its internal structure, or in other words, to the fact that the arrangement of the molecules is devoid of a centre, plane, or alternating axis of symmetry. The structure is of course the same for a given substance, whether hemihedral faces are developed or not. It has been discovered that most substances crystallising in enantiomorphous forms are endowed with optical activity, *i.e.*, the power of rotating the plane of polarised light. This property was found in quartz by Arago, and soon after it was proved by Herschel that a crystal having the development of Fig. 63 effects a clock-wise or *dextro* rotation, whilst the quartz of Fig. 64 is optically active in the opposite sense (*laevo*). Whether a given quartz crystal, devoid of hemihedral facets, is dextro or laevo can be easily settled by a simple optical determination.

The fact that certain enantiomorphous crystals are devoid of optical activity has received a satisfactory theoretical explanation, which cannot be entered into here. An example is sal-ammoniac (cubic system, class 29).

Certain substances preserve their optical activity when dissolved, liquefied, or vaporised: not so the remainder. An example of the first kind is tartaric acid; quartz and magnesium sulphate, on the other hand, are examples of the second kind. in the latter cases, the seat of the activity must lie in an enantiomorphous grouping of molecules in the crystal edifice. In the former case, the primary cause is evidently an enantiomorphous grouping of atoms within the molecule (see p. 209.)

Twin Crystals or Macles.—Sometimes two ("*twins*") or more ("*trillings*," "*fourlings*," &c.) crystals are grown together in a symmetrical manner, so that the various individuals present a recognisable regularity of orientation. Cassiterite, SnO_2, for example, often occurs in the elbow form of Fig. 65, which is clearly a combination of two crystals, each being the reflection of the other across a plane—"*twin plane*"—which happens to be the plane of contact. The couplet of fluorspar crystals (simple cubes of Fig. 66) is an interpenetration twin, and the orientation of one crystal is derivable from that of the other by a rotation of 180° about the diagonal emerging through the common corner; this direction of rotation is called the *twin axis.* Such groups of crystals are regarded as twins only

when the plane of reflection (or the axis of rotation) is parallel to a possible face (or a possible edge); any other groupings are regarded as accidental.

The twinning of enantiomorphous crystals deserves especial mention. Combinations are sometimes observed in which the two individuals are symmetrical about a plane. Now reflection of a dextro-crystal across a plane yields a laevo-crystal; such "twins," then, are really combinations of dextro- and laevo-individuals. If the two individuals interpenetrate each other

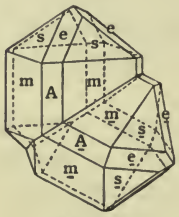


FIG. 65.

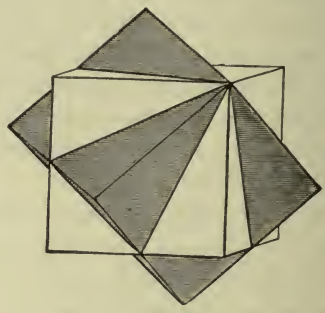


FIG. 66.

very thoroughly the result may appear to be a single crystal, and if the conditions have been favourable for the development of hemihedral facets, both sets will appear. This interesting property is of quite frequent occurrence in quartz, apparently single crystals of which sometimes exhibit both sets of x faces; when subjected to optical examination they are found to be composed of dextro- and laevo-material. Kipping and Pope[1] have shown that this mutual interpenetration provides a simple explanation of the general behaviour of "pseudo-racemic" substances.

OPTICAL, THERMAL, AND ELECTRICAL PROPERTIES OF CRYSTALS.

111 In general it may be stated that the physical properties of a crystal vary with the direction; but directions which are similar in the geometrical sense are also physically equivalent, so that the investigation of the physical properties often sheds valuable light on the symmetry.

[1] Kipping and Pope, *Journ. Chem. Soc.*, 1897, **71**, 989.

Optical Properties of Crystals.—The relations of crystals to light are of great importance, as enabling us to determine crystalline symmetry in cases in which the usual methods either give uncertain results or fail entirely. Transparent crystals belonging to the regular system exert no peculiar action on a ray of light; they behave in this respect like glass or any other amorphous substance. The incident ray gives rise to one refracted ray, and the crystal possesses one refractive index.[1]

All other crystals are doubly refractive, and they are further subdivided into uniaxial and biaxial crystals.

The uniaxial crystals comprise those of the rhombohedral, hexagonal and tetragonal systems. In one direction, termed the optic axis, which is parallel to the principal axis of symmetry, no double refraction occurs, but in all others the incident ray is doubly refracted, forming two plane-polarised rays, one of which, the ordinary ray, follows the ordinary law of refraction, whilst the other, the extraordinary ray, does not in general follow this law.

The biaxial crystals comprise those of the rhombic, monoclinic, and triclinic systems. In them, incident light is doubly refracted, yielding two extraordinary plane-polarised rays. They possess, however, two directions in which a ray is singly refracted, and these are called the optic axes. The angle between the optic axes of a biaxial crystal is an important constant of the crystal. Thus, for example, with sodium light it is 69° 5′ for rhombic sulphur, 47° 54′ for the monoclinic potassium magnesium sulphate, and 76° 36′ for the triclinic albite.

Thermal Properties.—Crystals which belong to the cubic system expand equally in every direction when heated, but for crystals belonging to other systems the expansion in general varies with the direction. A sphere cut out of a cubic crystal remains a sphere, but one cut out of a crystal belonging to the uniaxial systems (rhombohedral, tetragonal, and hexagonal) becomes an ellipsoid of rotation, the axis of rotation being coincident with the principal axis of symmetry; while in the case of the biaxial systems (rhombic, monoclinic, and triclinic), the sphere expands into an ellipsoid with three unequal, rectangular axes. As a result of the unequal expansion a small change is noted in at any rate some of the interfacial angles on raising the

[1] Cases have indeed been observed by Brewster and others in which a crystal belonging to the cubic system exhibits double refraction, but this is due to unequal tension in the mass of the crystal, and resembles the case of double refraction by unequally heated or compressed glass.

temperature. Cubic crystals, however, retain their angles unchanged.

Similar relationships hold good for heat conduction. The conducting power of crystals can be studied by covering the face of a crystal with a thin coating of melted wax, allowing the wax to solidify, and then bringing the point of a hot needle through the wax coating into contact with the crystal. If the crystals contain water of crystallisation, wax may be unnecessary (see p. 182). If the crystals conduct equally in all directions in the plane of the face, the wax will melt in a circle of which the hot point is the centre; this is the case with all cubic crystals. If the conduction be unequal, the melted wax assumes the form of an ellipse. The ellipses on similar faces have similar curvature and orientation.

Pyro-electric Behaviour of Crystals.—Certain badly conducting crystals when heated exhibit a peculiar development of electricity, one end of the crystal becoming negatively electrified, whilst the other end exhibits positive electricity. Such crystals are termed pyro-electric.

This phenomenon can naturally occur only in crystals which have no centre of symmetry, for the latter involves a similarity of physical properties in opposite directions along every line. If the polar ends of the crystal correspond to the two ends of an axis of symmetry, that axis is said to be polar. Polarity along an axis conclusively proves the absence of a plane of symmetry perpendicular thereto, and pyro-electricity is therefore a valuable help in the determination of symmetry. Examples of crystals possessing one polar axis are the minerals hemimorphite and tourmaline (classes 7 and 20 respectively); quartz exhibits three, and boracite four, polar axes.

Certain enantiomorphous crystals exhibit pyro-electricity, *e.g.*, tartaric acid (class 4); the dextro- and lævo-forms are antipodal with respect to their pyro-electric behaviour.

Reference List of the thirty-two Classes of Crystal Symmetry.

112 In the annexed list the following abbreviations are employed: "*II*-A" = a two-fold axis, "*III*-A" a three-fold axis, &c.; "*Alt*" = alternating, "*Pol*" = polar (used in connection with axes), "*P*" = plane of symmetry. The numbers refer to the number of planes or of axes of symmetry. Where

System.	Class No.[1]		Symmetry.	Example.
Triclinic .	*E.*	1	No symmetry	Calcium thiosulphate.
	Hol.	2	Centre of symmetry	Potassium dichromate.
Monoclinic		3	1*P*	Potassium tetrathionate.
	E.	4	1 II-*A* (*Pol.*)	Tartaric acid.
	Hol.	5	1 II-*A*, 1*P*	Rubidium magnesium sulphate.
Rhombic .	*E.*	6	(1+1+1) II-*A*	Magnesium sulphate.
		7	1 II-*A* (*Pol.*), (1+1)*P*	Hemimorphite, $ZnSiO_3$,$Zn(OH)_2$.
	Hol.	8	(1+1+1) II-*A*, (1+1+1)*P* . .	Potassium sulphate.
Tetragonal.	*E.*	9	1 IV-*A* (*Pol.*)	Barium antimonyl tartrate.
		10	1 IV-*A* (*Alt.*)	No example known.
	E.	11	1 IV-*A*, (2+2) II-*A*	Strychnine sulphate.
		12	1 IV-*A*, 1*P*	Scheelite, $CaWO_4$.
		13	1 IV-*A* (*Pol.*), (2+2)*P*	Iodosuccinimide.
		14	1 IV-*A* (*Alt.*), 2 II-*A*, 2*P* . . .	Urea.
	Hol.	15	1 IV-*A* (2+2) II-*A*, (1+2+2)*P*	Zircon, $ZrSiO_4$.
Rhombohedral .	*E.*	16	1 III-*A* (*Pol.*)	Sodium periodate.
		17	1 VI-*A* (*Alt.*)	Dioptase, CuH_2SiO_4.
	E.	18	1 III-*A*, 3 II-*A* (*Pol.*)	Quartz, SiO_2.
		19	1 III-*A*, 1*P*	No example known.
		20	1 III-*A* (*Pol.*), 3*P*	Tourmaline (complex silicate).
		21	1 VI-*A* (*Alt.*), 3 II-*A*, 3*P* . . .	Calcite, $CaCO_3$.
	Hol.	22	1 III-*A*, 3 II-*A*, 3*P*	Benitoite, $BaTiSi_3O_9$.
Hexagonal .	*E.*	23	1 VI-*A* (*Pol.*)	Strontium antimonyl tartrate.
	E.	24	1 VI-A, (3+3) II-*A*	Barium antimonyl tartrate + potassium nitrate.
		25	1 VI-*A*, 1*P*	Apatite, $Ca_5F(PO_4)_3$.
		26	1 VI-*A* (*Pol.*), 6*P*	Silver iodide.
	Hol.	27	1 VI-*A*, (3+3) II-*A*, (1+3+3)*P*	Beryl, $Be_3Al_2(SiO_3)_6$.
Cubic . .	*E.*	28	4 III-*A*, 3 II-*A*	Sodium chlorate.
	E.	29	4 III-*A*, 3 IV-*A*, 6 II-*A*	Sal-ammoniac.
		30	4 III-*A*, 3 II-*A*, 3*P*	Iron pyrites, FeS_2.
		31	4 III-*A* (*Pol.*), 3 II-*A*, 6*P* . . .	Zinc blende, ZnS.
	Hol.	32	4 III-*A*, 3 IV-*A*, 6 II-*A*, (3+6)*P*	Fluorspar, CaF_2.

[1] The numerical order of the classes is that adopted by Tutton in his *Crystallography and Practical Crystal Measurement*, p. 143 (Macmillan, 1911).

there are several planes of symmetry they are divided up into groups, the members of each group occupying similar positions in the crystal; thus, $(3+1)P$ signifies that there are altogether four planes of symmetry, three of which are similar (*i.e.*, are parallel to faces belonging to the same form), but different from the fourth. The same procedure is adopted for the axes. Those eleven classes in which enantiomorphism is possible are indicated by the letter *E*. The class in each system with highest symmetry is often termed *holohedral* ("*Hol*") since the number of faces belonging to each form is the greatest possible.

POLYMORPHISM.

113 In his celebrated system of classifying minerals devised in 1801, Haüy propounded the following two principles; (1) a given substance always crystallises in the same form, (2) similarity of form of two substances, except in crystals of the cubic system, indicates a complete identity of chemical composition. It was, however, soon found that his principles could not be applied in all their generality, for exceptions to both of these statements were known even at that time, and many more were soon discovered and established by careful investigation.

In 1821, Mitscherlich proved that the property of crystallising in two distinct forms, *i.e.*, forms which are not referable to the same parameters, is common to many substances both elementary and compound, and he termed such substances *dimorphous*.

It has since been found that other substances are capable of existence in three or even four distinct crystalline forms, as, *e.g.*, titanium dioxide and ammonium nitrate respectively. These are termed *trimorphous* and *tetramorphous*, whilst the general term *polymorphous* is applied to all substances which possess more than one crystalline form.

The different modifications of polymorphous substances are not only distinguished by their crystalline form, but also differ in their other physical properties, such as specific gravity, hardness, cleavage, refractive power, &c. In fact, they behave physically like distinct substances. These differences, however, exist only in the crystalline condition, the various forms yielding identical solutions, melts, and vapours. The differences therefore would seem to be due solely to a difference in the arrangement of the chemical molecules in the crystal structure. Substances of the

same composition which preserve their individuality when dissolved are not polymorphous modifications but *isomerides*.

Sulphur is an excellent example of a polymorphous substance. At least four crystalline modifications are known, as well as several amorphous varieties; only two of the crystalline modifications will be considered. One of these occurs in nature, and is rhombic (class 6), with $a:b:c=0{\cdot}8130:1:1{\cdot}9030$ (Fig. 67), the specific gravity being 2·07. It is also formed on evaporation of a solution at the ordinary temperature. The second modification was discovered by Mitscherlich by allowing fused sulphur to cool; it is monoclinic (class 5), with $a:b:c=0{\cdot}9958:1:0{\cdot}9998$; $\beta=95°46'$, and the specific gravity is 1·96 (Fig. 68). The rhombic form is stable at the ordinary temperature, but at 95·6° it changes with absorption of heat

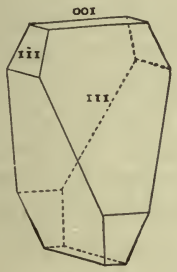


Fig. 67.

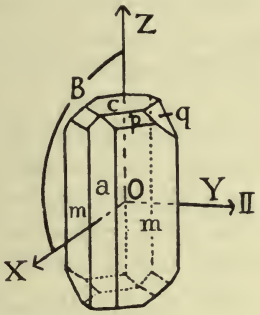


Fig. 68.

into the monoclinic variety, which is stable from this temperature up to the melting point. The reverse change, accompanied by evolution of heat, occurs when the monoclinic crystals are cooled below 95·6°. This "transition temperature" is influenced by change of pressure, and Tammann[1] has found that under a pressure of 1288 atmospheres the transition point is 151°. This is also the melting point of the monoclinic modification under the pressure mentioned, so that under higher pressures and temperatures it ceases to have any stable existence. Similar cases are known in which under the ordinary atmospheric pressure the transition temperature is above the melting point of one of the two modifications.

The exceptions to Hauy's second statement are isomorphous substances (page 211).

[1] Tammann, *Ann. Physik*, 1899, [3], **68**, 633.

CRYSTALLOCHEMICAL ANALYSIS.

114 Since, with the exception of substances belonging to the cubic system, no two substances are alike, the possibility of identifying a given unknown substance by measurement becomes obvious, provided the substance has already been examined crystallographically. Such a process of identification has been termed "Crystallochemical Analysis" by Fedoroff,[1] who has succeeded in classifying all the available crystallographic material so as to permit of easy reference. The classification depends on the principle that the angles in the most important zone of a crystal approximate either to 90° or to 60°, or in other words crystals are either pseudo-tetragonal or pseudo-hexagonal. A good example is potassium dichromate, which is triclinic with $a:b:c=1{\cdot}0116:1:1{\cdot}8146$; $\alpha=98°\,0'$, $\beta=96°\,13'$, $\gamma=90°\,51'$. Now these values are not far removed from the hypothetical values, $1:1:1{\cdot}8146$; $\alpha=\beta=\gamma=90°$, which would be characteristic parameters for a tetragonal crystal. Each substance hitherto measured (the total being about ten thousand) has been given a "correct setting," *i.e.*, has been set up so that the important 90° or 60° zone is placed in the vertical direction. An index of all these correct settings has been compiled, the values of certain characteristic angles, never exceeding five in number and usually only two or three, being taken as the basis of the sub-arrangement.

An unknown substance can be quickly identified by measuring one or two crystals; an examination of the various angles leads to the discrimination of the correct setting, and the characteristic angles can then be selected. A substance having these angles is sought for in the index, and identification is effected. Apart from its great theoretical interest, the new method is likely to be of the utmost practical utility, especially in those cases where only a small amount of material is available. The index will be published in the year 1914.

CRYSTAL STRUCTURE.[2]

115 The first real theory of crystal structure is due to Haüy, who advanced the idea that a crystal is built up of minute

[1] Fedoroff, *Zeit. Kryst. Min.*, 1912, **50**, 513; Barker, *Chem. News*, 1912, **106**, 199.

[2] Consult *Brit. Assoc. Report*, 1901, 297.

units having the form of the cleavage figure, and packed together so as to fill space completely. The structure of a crystal of sodium chloride on this theory is shown in Figs. 69 and 70, which illustrate also the development of an octahedral facet at one of the corners. This and other inclined facets present a step-like character which distinguishes them from those containing the faces of the cubelets. As the irregularity

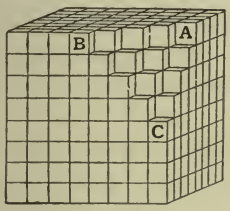


FIG. 69.

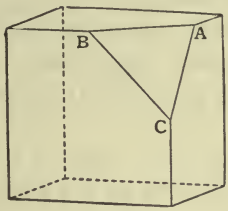


FIG. 70.

is of molecular dimensions, no experimental evidence of this distinction is looked for.

Now it is extremely unlikely that the whole space is occupied by actual matter, the physical properties of crystals pointing rather to discontinuity of structure. If each cubelet be replaced by a molecule represented by a point placed at its centre, the "space lattice" structure of Fig. 71 is obtained.

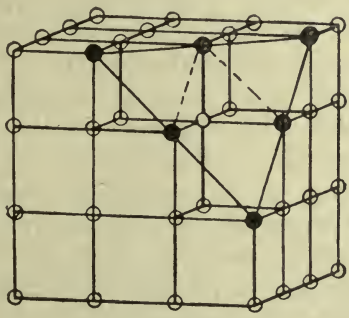


FIG. 71.

This removes the distinction between cube faces and other faces just referred to; all are alike formed by drawing planes through parallel files of points. The faces differ, however, in two respects, (1) in the pattern presented by the points of a plane, which is square in the cube planes and rhombic in the octahedral planes, (2) in the density with which the plane is beset with points, the density being greater in the cube than in the octa-

hedral plane. It has been suggested that the directions of cleavage have some relation to this "reticular density."

The various space lattices were studied thoroughly by Bravais, who showed that fourteen types are distinguishable, falling under the seven crystalline systems. The symmetry, however, is always that of the holohedral class of each system; thus the existence of the lower classes of symmetry necessitates a further assumption. Bravais met the requirement by employing small symmetrically shaped particles instead of mere points, the shape and orientation of these particles being such as to produce the lowering of symmetry requisite in each case.

Subsequent workers have shown not only that it is possible to account for all the thirty-two classes without having recourse to Bravais particles, but also that a new method of treatment reveals possible cases of crystal structure which are not capable of representation by his method. There are two stages in this final development.

The first advance is due in its completed form to Sohncke.[1] It will be observed that the space lattice is homogeneous, every part of the structure being the same as any other part. Sohncke showed that sixty-five types of arrangement of points in space ("point-systems") are possible which fulfil the following definition of "homogeneity"; the system of points, regarded as unlimited, is such that the arrangement around any one of the points is the same as around any other.

The second and final advance consisted in enlarging Sohncke's definition of homogeneity in the following sense: the assemblage around a selected point may be the same as, or the mirror image of, the assemblage around other points. By introducing this principle of enantiomorphous similarity, it was discovered independently by Fedoroff, Schoenflies, and Barlow[2] that there are in all 230 generalised types of point systems, which can be allocated to the thirty-two classes according to their symmetry.

The geometrical investigation of the possible types of arrangement of the molecules in crystals may be regarded as final. The discovery of the particular arrangement which holds

[1] Sohncke, *Entwickelung einer Theorie der Krystallstruktur*, Leipzig, 1879; *Zeit. Kryst. Min.*, 1888, **14**, 423.

[2] Consult H. Hilton, *Mathematical Crystallography* (Oxford, Clarendon Press, 1903).

for any given crystal is a much more difficult matter (see page 220).

A remarkable optical indication of the existence of a regular space lattice structure in crystals has been recently furnished by Laue, Friedrich, and Knipping.[1] The distance between contiguous molecules in a space lattice has been calculated to be of the order 10^{-8} cm., whilst the wave-length of Röntgen rays is less, being of the order 10^{-9} cm. A photograph of a circular beam of Röntgen rays which has passed through a crystal shows not only a round central dark spot, corresponding to the undeviated beam, but also surrounding it a number of smaller patches

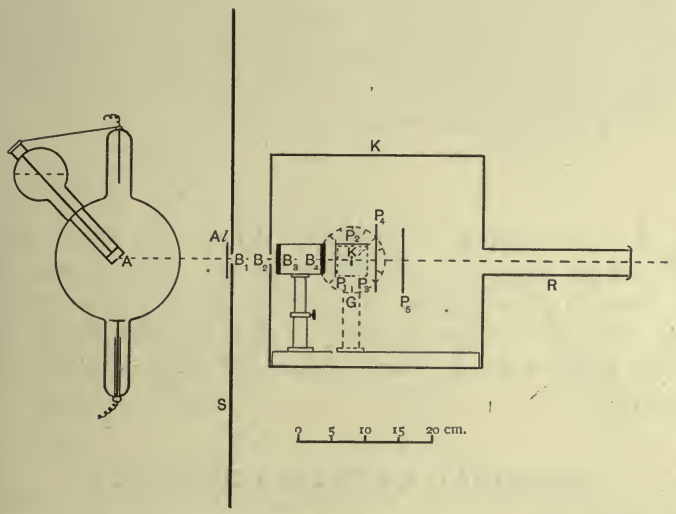


Fig. 72.

which are due to secondary rays set up in the crystal. The apparatus used is shown in Fig. 72, where A is the X-ray tube, $B_1 - B_4$ diaphragms allowing a narrow beam of rays about 0·75 mm. diameter to fall on the crystal Kr which is adjusted on a goniometer. The screen S and the box K are made of lead. The photographic plates were placed in positions $P_4 - P_5$ and treated to a very long exposure.

The results obtained from sections of zinc blende, ZnS, parallel respectively to the cube and octahedral planes, are reproduced in Figs. 73 and 74. The symmetry in the first figure consists of four planes of symmetry intersecting at angles

[1] *Sitz. Bayer. Akad. Wiss.*, June 8th, 1912, pp. 303, 363.

of 45°, and an axis of four-fold symmetry. In the second figure there are three planes of symmetry intersecting at 120°, and a three-fold axis of symmetry. Now this symmetry is precisely that which a cubic space lattice would exhibit when viewed perpendicularly to a cube and an octahedral face respectively,

Fig. 73.

Fig. 74.

and the photographs undoubtedly reveal the space lattice nature of the structure. It is perhaps too early to state the full meaning of the result. A possible interpretation appears to be that each separate patch is due to deflection of the original beam of rays by parallel planes of particles in the space lattice.

CHEMICAL CRYSTALLOGRAPHY.

116 The study of the correlation of chemical composition with crystalline form and structure is a subject of great interest, and is termed chemical crystallography. Any change in the arrangement of the atoms in the molecule (isomerism) is found to lead to a profound difference in the form of the crystals; more than this, under different conditions of temperature and pressure one and the same compound may crystallise in entirely different forms (polymorphism). These two facts go far to prove that the crystalline form is a highly constitutive property, and is a direct outcome of the forces mutually operative between the various atoms in the molecule. This deduction is confirmed by the observation that the closer the chemical similarity of two given compounds, the more striking is the similarity of crystalline form: optical antipodes crystallise in enantiomorphous

forms: substances of very similar composition and constitution generally yield "isomorphous" crystals (see p. 211); and, in other cases where the chemical similarity is less pronounced, certain relationships may yet be found between the crystalline forms of the compounds ("morphotropy," p. 219).

The subject of chemical crystallography has engaged the attention of investigators since comparatively early times, and a vast amount of material has been accumulated. Considerable advances have been made recently in the study of the dependence of the crystal structure on chemical composition, as a result of the interesting theoretical work of Barlow and Pope, and of Sollas, and it would appear reasonable to hope that further work on the same lines will ultimately lead to far-reaching extensions of stereochemical knowledge.[1]

Enantiomorphism of Molecule and of Crystalline Form.— Although it had long been recognised that optical activity is

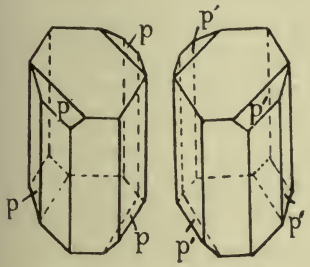


Fig. 75. Fig. 76.

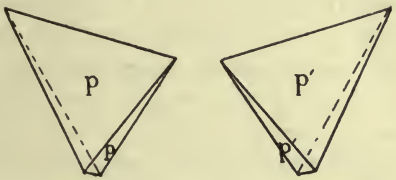


Fig. 77. Fig. 78.

the result of a certain asymmetry of arrangement, the greatest discovery of all was reserved for Pasteur, who in the year 1848 showed that substances endowed with optical activity in solution crystallise in enantiomorphous forms. He also recognised that in such cases the seat of the optical activity lies in the unsymmetrical character of the atomic groupings in the chemical molecule. On allowing the sodium ammonium salt of racemic acid to crystallise, the two kinds of crystals of Figs. 75 and 76 were deposited, which could be distinguished by means of the hemihedral facets *p* and *p′*, and separated from each other. On dissolving in water, the two kinds of crystals gave oppositely

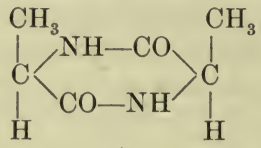
[1] For further information on this subject, see Fock, *An Introduction to Chemical Crystallography*, translated by W. J. Pope (Oxford, Clarendon Press, 1895); Groth, *Einleitung in die chemische Krystallographie* (Leipzig, Engelmann, 1904); English translation by H. Marshall (Gurney, 1906); also Barker, *Chemical Crystallography* (Longmans, 1913).

active solutions, from one of which Pasteur obtained ordinary *d*-tartaric acid, but from the other a new acid—*l*-tartaric acid.

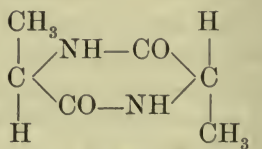
It was suggested by Pasteur that the atomic grouping is of a spiral or, perhaps, tetrahedral character. The latter idea may have been suggested to him by the fact that the hemihedral facets of Figs. 75 and 76, when extended in space, form the tetrahedra of Figs. 77 and 78, one of which is the non-superposable mirror image of the other.

Somewhat later, by giving a spacial extension to the Kekulé hypothesis of quadrivalent carbon, it was pointed out by van't Hoff and Le Bel independently that the enantiomorphous character of the molecular configuration of tartaric acid, as well as that of many other optically active organic compounds, is due to the presence of one or more "asymmetric" carbon atoms, *i.e.*, atoms directly combined to four dissimilar groups. Further, the asymmetric carbon atom may be supposed to be placed at the centre of a tetrahedron, the four groups being at the corners. Subsequently, optically active compounds containing selenium, tin, sulphur, phosphorus and nitrogen united to different groups have been obtained, and there has been a disposition to ascribe the activity to the presence of the asymmetric atoms. A more satisfactory view, however, is to ascribe the activity to the enantiomorphous configuration of the molecule as a whole. Optically active compounds have been prepared by Werner[1] which, perhaps, do not contain an asymmetric atom, *e.g.*, potassium chromium oxalate, $K_3Cr(C_2O_4)_3,H_2O$; the atomic configuration, however, is of such a character that it is non-superposable on its mirror image.

The true test for enantiomorphism of molecular structure is not the presence or absence of any particular atom united to dissimilar groups, but the absence of plane, centre, and alternating axes of symmetry in the molecule as a whole, the presence of any one of these elements of symmetry being sufficient to cause identity of the molecule with its mirror image. For example, 1 : 4-diketo-2 : 5-dimethylpiperazine[2] exists in two forms, *cis-* and *trans-* :—



cis.



trans.

[1] *Ber.*, 1912, **45**, 3061.

[2] Fischer, *Ber.*, 1906, **39**, 467, 3981.

Now the *cis*-form only possesses a two-fold axis and has therefore a non-superposable mirror image; but the *trans*-form, although devoid of a plane of symmetry, has a centre of symmetry since a line passing through the centre of the ring meets similar groups or atoms at the two ends (the carbonyl oxygen and the imido-nitrogen being in the plane of the ring). The former exists in two optically active forms, the latter does not.

The numerical values of all properties of antipodal crystals are identical; thus, the specific gravity, molecular volume, and refractive indices are the same, as well as the angles and the parametral ratios; and it is only by means of such properties as pyro-electricity, the sign of the rotatory power, the development of hemihedral facets, and the orientation of etched figures that the crystals can be distinguished.

Racemic substances, or compounds of the two antipodes in equal molecular proportions, do not bear a very close crystallographic relationship to the antipodes themselves; in some cases, however, morphotropic resemblances appear to exist, as has been pointed out especially by Jerusalem.[1]

Pseudo-racemic compounds have practically the same parameters as the pure antipodes, and are to be looked upon as mixed crystals or intimate intercalations of active material of the two kinds (see p. 198).

117 *Isomorphism.*—Haüy's second principle, that identity of crystalline form implies identity of composition, was soon found to be inconsistent with facts. As long ago as 1784, Leblanc had shown that crystals of an identical form could be obtained from solutions containing sulphate of copper and sulphate of iron mixed in very different proportions. He likewise states that crystals of alum, a sulphate of aluminium and potassium, may frequently be found to contain a considerable quantity of iron, although no alteration in the crystalline form can be noticed. Vauquelin, too, showed in 1797 that common potash alum may contain large quantities of ammonium, and yet the crystalline form of the substance does not undergo any change. It is well known also that many minerals which are identical in crystalline form may possess a very different chemical composition. Thus the common garnet, crystallising in the cubic system, sometimes contains much iron and little aluminium and sometimes large quantities of aluminium and little iron.

[1] *Journ. Chem. Soc.*, 1912, **101**, 1268.

Berthollet considered facts like these to be in accordance with his views on chemical combination, but Proust explained them by supposing that we have here to deal, not with chemical compounds, but rather with mechanical mixtures.

In the year 1816, Gay-Lussac made the remarkable observation that when a crystal of common potash alum is suspended in a saturated solution of ammonia alum it grows exactly as if it had been placed in the solution from which it was originally obtained. From this fact he drew the conclusion that the molecules of these two alums possess the same form. Later on, in 1819, Beudant noticed that if solutions containing two of the following salts, sulphate of zinc, sulphate of iron, or sulphate of copper, are crystallised, the deposited crystals always possess the form of one of these salts, although they contain a considerable quantity of the other salt, which, when crystallised by itself, possesses a totally different form.

In order to explain these and similar well-recognised facts Haüy supposed that certain substances possess the power of crystallisation to such a degree that even when present in small quantities they compel other substances to adopt their crystalline form.

Clear light was thrown on this subject by the researches of Mitscherlich, published in 1819. Mitscherlich showed that the compounds of various elements possessing a similar composition have also identical crystalline form, as ascertained by the measurement of their angles. The first substances examined by Mitscherlich were the arsenates and phosphates of sodium, potassium and ammonium. He showed not only that the crystals of the phosphate and arsenate of the same metal contain the same amount of water of crystallisation, and crystallise in the same form, but also that when the two salts are mixed in varying quantities the crystals which such solutions deposit are of the same form as those obtained from solutions of the pure salts, whilst the proportions of the ingredients in the crystal vary according to their proportions in the solution. Hence Mitscherlich concluded that analogous elements or groups of elements can replace one another in compounds without any alteration of crystalline form. Such substances are said to be *isomorphous* (ἴσος, equal, μορφή, shape). Many other compounds were shown by Mitscherlich to conform to the above law.

Mitscherlich was at first of the opinion that the geometrical similarity of isomorphous substances is complete, that is, that

they have absolutely the same angles. He was not aware of the work of Wollaston,[1] who some seven years previously had measured very carefully the rhombohedral cleavage angle of the following naturally occurring carbonates and obtained the values:—calcite, $CaCO_3 = 74°55'$; dolomite, $CaMg(CO_3)_2 = 73°45'$; and spathic iron ore, $FeCO_3 = 73°0'$. All subsequent measurements have confirmed these values, and they are the ones actually accepted at the present day. After obtaining a Wollaston goniometer, Mitscherlich found that isomorphous substances are not identical, but merely very similar, in angles. All subsequent work has confirmed this view, except, of course, in the case of cubic substances, the angles of which are constant for all, being, in fact, determined by the symmetry.

118 *The Relation of Isomorphism to Chemical Constitution.*—The necessity for a similar arrangement of atoms in the molecules of isomorphous compounds was appreciated by Mitscherlich, but its full importance became apparent only after the development of the structure theory—a product of organic chemistry which was subsequently applied to inorganic substances. It was recognised that isomorphous substances have a similar atomic arrangement: for example, the constitutional formulæ of potassium sulphate and selenate are completely analogous. The formulation of the periodic classification provided a further stimulus to the study of isomorphism. It now became evident that in most simple isomorphous compounds the replaceable elements belong to the same sub-group of Mendeléeff's arrangement, *e.g.*, potassium, rubidium, and cæsium; chlorine, bromine, and iodine; iron, nickel, and cobalt. In the more complicated compounds, however, especially in the large class of double salts, a considerably greater degree of freedom exists: elements which are not in the same sub-group of the periodic classification can replace each other isomorphously, provided that the degree of oxidation (valency) is the same, *e.g.*, the metals copper, zinc, cadmium, manganese, iron, nickel, and cobalt are capable of isomorphously replacing the metal magnesium in rubidium magnesium sulphate (see p. 189).

The very striking similarity of calcite and sodium nitrate has long been known, but as a direct result of the development of the structure theory in chemistry there has been a tendency to dispute the isomorphism on account of the dissimilarity of

[1] *Phil. Trans.*, 1812, **102**, 159.

constitution when the two compounds are formulated on the conventional lines of valency, viz.,

$$O=C<\begin{matrix}O\\O\end{matrix}>Ca \qquad \begin{matrix}O\\O\end{matrix}\gg N-O-Na.$$

It has, however, been pointed out [1] that this case is by no means isolated, for there are many other isomorphous series of compounds which present similar peculiar features of chemical constitution. The following four series will serve as illustrations:

Tetragonal System.		
Potassium periodate (Fig. 35, p. 183)	KIO_4	$a:c = 1:1{\cdot}5534.$
Scheelite (calcium tungstate)	$CaWO_4$	$= 1:1{\cdot}5268.$
Potassium osmiamate	$KOsO_3N$	$= 1:1{\cdot}6319.$
Rhombic System.		
Potassium perchlorate (Fig. 47, p. 190)	$KClO_4$	$a:b:c = 0{\cdot}7817:1:1{\cdot}2792.$
Barytes (barium sulphate)	$BaSO_4$	$= 0{\cdot}8152:1:1{\cdot}3136.$
Potassium borofluoride	KBF_4	$= 0{\cdot}7898:1:1{\cdot}2830.$
Rhombic System		
Potassium sulphate (Fig. 44, p. 189)	K_2SO_4	$a:b:c = 0{\cdot}5727:1:0{\cdot}7418.$
Potassium glucinum fluoride	K_2BeF_4	$= 0{\cdot}5708:1:0{\cdot}7395.$
Tetragonal System.		
Xenotime	YPO_4	$a:c = 1:0{\cdot}6177.$
Zircon (Fig. 48, p. 191)	$ZrSiO_4$	$= 1:0{\cdot}640.$
Cassiterite or tinstone	SnO_2 or $SnSnO_4$	$= 1:0{\cdot}6726.$

It will be seen that although in each series there is a complete analogy of composition with respect to the total number of the atoms in the molecule, yet the constitutions as ordinarily accepted are quite different. A possible explanation appears to be that the theory of coordination advanced by Werner is applicable to the compounds enumerated.

119 *Mutual Affinities of Isomorphous Substances.*—It has been mentioned that all cubic substances are isomorphous in the literal sense of the word, but to designate substances like alum and potassium platinichloride isomorphous, merely because they both crystallise in regular octahedra, would be entirely misleading. On this account the term isomorphism has long been restricted to those substances whose similarity of form is unquestionably due to a far-reaching similarity of internal structure, which is in turn the result of a close correspondence of atomic and molecular constitution. Owing to the similarity of structure, isomorphous compounds in this narrow sense are endowed with very special properties: (1) they form mixed crystals or isomorphous mixtures in variable proportions; (2)

[1] Barker, *Journ. Chem. Soc.*, 1912, **101**, 2484.

they are capable of forming regular overgrowths or "parallel growths" on each other; (3) a crystal fragment, when introduced into a supersaturated solution of another substance isomorphous with it, immediately relieves the supersaturation and causes a copious separation of crystals.[1] These three properties have been employed to test the character of the isomorphism in suspected cases, but recent investigations have proved that pairs of admittedly isomorphous substances fail to respond to the three tests when the molecular volumes are not sufficiently close in value.

Isomorphous Mixtures.—The properties of isomorphous mixtures are a continuous function of the percentage composition (Retgers), and in many cases this function is practically linear; so that the values of a property of the mixture can be very simply calculated. Many isomorphous substances, however, are not miscible in every proportion, each being capable of taking up only a limited amount of the other; others, again, do not mix at all. Thus, according to Wulff,[2] ammonium sulphate (molecular volume = 74·63) mixes in all proportions with rubidium sulphate (73·77), and also completely with potassium sulphate (65·33) and with cæsium sulphate (85·17). Potassium and cæsium sulphates, however, are completely immiscible.

Parallel Growths.—This subject has been especially studied by Barker,[3] who in addition to observations on many other substances has found that potassium and cæsium sulphates yield quite irregular deposits on each other, whilst all other possible pairs of the sulphates mentioned above always give parallel growths.

Relief of Supersaturation.—Our knowledge concerning the state of supersaturation has been greatly enlarged by the work of Miers and Isaac,[4] who from observations of the change of refractive index of a cooling, supersaturated, solution have arrived at the conclusion that there are two states of supersaturation, viz., the *metastable* and the *labile* states. A solution in the metastable

[1] Gernez, *Compt. rend.*, 1865, **60**, 833, 1027; 1866, **63**, 843; Lecoq de Boisbaudran, *Ann. Chim. Phys.*, 1866, [4], **9**, 173; Thomson, *Journ. Chem. Soc.*, 1879, **35**, 196; Thomson and Bloxam, *ibid.*, 1882, **41**, 379.

[2] Wulff, *Zeit. Kryst. Min.*, 1906, **42**, 558.

[3] Barker, *Journ. Chem. Soc.*, 1906, **89**, 1120; *Min. Mag.*, 1907, **14**, 235; 1908, **15**, 42.

[4] Miers and Isaac, *Journ. Chem. Soc.*, 1906, **89**, 413; Isaac, *ibid.*, 1908, **93**, 384.

condition, although supersaturated, is not capable of crystallising spontaneously (*i.e.*, unless inoculated with a crystal of the solute), no matter how violently it is agitated. If the solution is protected from the introduction of crystal nuclei from outside, it will on further cooling pass into the labile condition and crystallise spontaneously. A sudden shower of crystals then appears, the shower being preceded by a sudden fall in the value of the refractive index of the solution.

Miers and Chevalier have found that calcite (molecular volume = 36·8) induces crystallisation in a metastable solution of sodium nitrate (37·8), whilst the remaining rhombohedral carbonates (see below), with molecular volumes ranging between 28·2 and 31·0, have no action.

Isomorphous Mixtures in Minerals.—Cases of isomorphous mixtures are very common among minerals, and the following serve as an excellent illustration of isomorphous replacement:—

Apatite (Fig. 36)	$Ca_5F(PO_4)_3$
Pyromorphite	$Pb_5Cl(PO_4)_3$
Mimetite	$Pb_5Cl(AsO_4)_3$
Vanadinite	$Pb_5Cl(VO_4)_3$.

The isomorphously replaceable chemical elements in these minerals are:—

(1) Phosphorus, Arsenic, Vanadium; (2) Calcium and Lead; (3) Chlorine and Fluorine. Not infrequently both chlorine and fluorine occur in the same specimen of apatite, and phosphorus and arsenic often replace one another in pyromorphite.

Another well marked case is that of the rhombohedral carbonates of the metals calcium, magnesium, iron, zinc, and manganese. These minerals all crystallise in similar rhombohedra, the values of the rhombohedral angle between cleavage planes being:—

Calcium carbonate, or calcite, $CaCO_3$	74° 55′
Magnesium carbonate, or magnesite, $MgCO_3$ . .	72° 35′
Ferrous carbonate, or spathic iron ore, $FeCO_3$.	73° 0′
Zinc carbonate, or calamine, $ZnCO_3$	72° 20′
Manganese carbonate, or diallogite, $MnCO_3$ . .	73° 55′.

The various metals enumerated can replace each other in varying proportions, as is well illustrated by the following percentage analysis of spathic iron ore:—

Ferrous oxide, FeO	45·55
Manganese oxide, MnO	12·50
Lime, CaO	1·57
Magnesia, MgO	1·80
Carbonic acid, CO_2	38·58
	100·00

If we now divide the percentage of oxide by its combining weight, thus $\frac{45{\cdot}55}{71{\cdot}84}$ for ferrous oxide, &c., &c., we obtain the following numbers representing the proportion between the number of equivalents of the several constituents present :—

FeO = 0·6340, MnO = 0·1762, CaO = 0·0280, MgO = 0·0446.

The sum of these amounts (0·8828) is, however, very nearly the proportion which must be present in order to unite with $\frac{38{\cdot}58}{44{\cdot}00} = 0{\cdot}8768$ equivalent of CO_2, the difference being due to errors of experiment. In other words, the number of molecules of the basic oxides present is the same as that of the carbon dioxide ; hence the formula for the spathic iron ore may be written (Fe,Mn,Ca,Mg)CO_3, signifying that the relative quantities of the metals in question present are indeterminate, but are in the aggregate such as are needed to combine with CO_2. Hence we have the following as the composition of the mineral :—

Ferrous carbonate, $FeCO_3$	73·45
Manganese carbonate, $MnCO_3$ . . .	20·25
Calcium carbonate, $CaCO_3$	2·80
Magnesium carbonate, $MgCO_3$ . . .	3·76
	100·26

120 *Comparison of Isomorphous Substances by means of Topic Axes.*—The parametral ratios of a crystal furnish merely the relative lengths of the three edges of Haüy's structural unit, the actual lengths themselves remaining unknown. It has been ingeniously suggested by Becke[1] that in the case of two isomorphous substances the volumes of Haüy's units are proportional to the molecular volumes, *i.e.*, the molecular weight divided by the specific gravity. The volumes and also the ratios

[1] Becke, *Anzeiger Akad. Wiss. Wien*, 1893, **30**, 304.

of the edge-lengths of the units being known, it is a simple matter to calculate the edge-lengths themselves; these three lengths are termed the *topic parameters* or *topic axes*, and are denoted by the letters χ, ψ, ω. When the pile of units is supposed to be replaced by molecular points at their centres, so that the structure becomes a space lattice, the topic axes then represent the distances between contiguous molecules in the three principal directions of the structure.

The following table includes the topic axes of the isomorphous series consisting of the sulphates of potassium, rubidium, cæsium, and ammonium, which have been very carefully investigated by Tutton.[1] One of the most important results of the investigations of this author is that, with regard to the geometrical and general physical properties, the rubidium compounds take up an intermediate position between the corresponding compounds of potassium and cæsium.

Crystallographic axes, $a : b : c$.	Density	Mol. vol.	Topic Axes.		
			χ	ψ	ω
K_2SO_4 . . . . 0·5727 : 1 : 0·7418	2·666	64·91	3 8810	3·8574	4·9964
Rb_2SO_4. . . . 0·5723 : 1 : 0·7485	3·615	73·34	4·0304	4·0039	5·2366
Cs_2SO_4 . . . . 0·5712 : 1 : 0·7531	4·246	84·58	4·2187	4·1849	5·5175
$(NH_4)_2SO_4$ . . 0·5635 : 1 : 0·7319	1·772	74·04	4·0792	4·0051	5·2020

It is interesting to note that the effect on the structure of the crystal of replacing the potassium atom by the ammonium radical, NH_4, is almost exactly the same as that produced by its substitution by rubidium.

The values of the topic axes shed some light on the relations of the first three salts with respect to miscibility and capacity of forming parallel growths. It must be inferred that these two properties depend on the possibility of a fitting together of the two structures—in no other way does the rôle played by the molecular volume admit of interpretation. The large difference between the molecular volumes of the potassium and cæsium salts leads to correspondingly large differences in the values of the topic axes, which, it will be remembered, furnish a measure of the relative distances between contiguous molecules of the space lattices. Apparently these differences have over-

[1] See Tutton, *Crystalline Structure and Chemical Constitution* (Macmillan, 1910).

stepped the limit of mutual accommodation and the two substances will neither mix nor form parallel growths. The limit is not exceeded, however, when either the rubidium or the ammonium salt is compared with the potassium and cæsium salts. These considerations illustrate the value of the conception of topic axes in comparisons of the members of an isomorphous series.

Isodimorphism.—When two substances are isomorphous with one another and one of them is dimorphous, crystallising in two distinct forms, it is often found that the second substance is also dimorphous, and that each of its two forms corresponds with one of the forms of the first substance, a double isomorphism being thus exhibited. Such substances are said to be *isodimorphous*, and cases of *isotrimorphism* are also known. The trioxides of arsenic and antimony serve as a striking example of isodimorphism. For a long time these compounds were known to occur only in forms which were not isomorphous, and this was the more remarkable as their elementary constituents exhibit such a close analogy. It was afterwards found that arsenious oxide, As_4O_6, which usually crystallises in regular octahedra (arsenolite), is occasionally met with in rhombic crystals (claudetite), exactly identical in form with those in which antimonious oxide, Sb_4O_6, commonly occurs in nature (valentinite). A mineral consisting of this latter oxide, and called senarmontite, was next discovered. The crystals of this are octahedral, so that the isodimorphism of these substances is now completely proved, especially since it has been found possible to produce the octahedral crystals of antimonious oxide artificially.

Morphotropy.—The term "morphotropy" really connotes the general study of the variation of crystal form with a specific change of chemical composition, of which enantiomorphism and isomorphism are but particular cases. By many authors, however, it is used in connection with resemblances between compounds not usually regarded as isomorphous, either because the substances are not of "analogous" composition, or because the degree of resemblance is fairly remote. No hard and fast line can be drawn between isomorphous and morphotropic similarity.

A good example of a morphotropic series has been investigated by Slavik,[1] viz., ammonium iodide and tetramethyl (-ethyl

[1] Slavik, *Zeit. Kryst. Min.*, 1902, **36**, 268.

and -propyl) ammonium iodides. The first mentioned is cubic with a perfect cubic cleavage, the second tetragonal, also with three cleavage directions mutually perpendicular, the third tetragonal, but with a different cleavage, and the fourth rhombic. A comparison of the topic axes will show the change in the molecular spacing along the directions of the three crystallographic axes induced by the introduction of the alkyl groups.

Crystallographic axes, $a:b:c$.		Mol. vol.	Topic axes.		
			χ	ψ	ω
NH_4I	1 : 1 : 1	57·5	3·860	3·860	3·860
$N(CH_3)_4I$ . . .	1 : 1 : 0·7223	108·7	5·319	5·319	3·842
$N(C_2H_5)_4I$ . . .	1 : 1 : 0·5544	162·9	6·648	6·648	3·686
$N(C_3H_7)_4I$ . .	0·7761 : 1 : 0·6283	235·9	6·093	7·851	4·933

MECHANICAL THEORIES OF CRYSTAL STRUCTURES.

121 Frequent attempts have been made in the past to explain the form and general physical properties of a crystal by a mechanical arrangement of the various atoms and molecules, but they have not met with any general success. Quite recently, however, the theories of Barlow and Pope, and of Sollas, have very deservedly attracted considerable attention on account of the great measure of success attained, although the initial assumptions are few in number, and of a simple and reasonable character.

Valency Volume Theory of Barlow and Pope.[1]—The fundamental assumption of these authors is that the volumes of space occupied by the various atoms in a given molecule are approximately proportional to the valencies of the atoms. Whenever an element exhibits more than one kind of valency, one of these, generally the lowest, is selected; *e.g.*, the volume of an atom of nitrogen is always taken to be three times, and that of sulphur twice, the volume of an atom of hydrogen.

In working out the structural details it is found simplest to consider the atoms, supposed incompressible, though capable of elastic deformation, as initially spherical. When the spheres

[1] W. J. Pope, *Chemical Society's Report on Crystallography*, 1908.

have been packed together subsequent compression of the assemblage may be supposed to squeeze out the interstitial space, whereby the spheres are transformed into plane polyhedral bodies, as a result of the flattening that will occur at every point of contact. If the original assemblage of spheres is packed as closely as possible, the subsequent deformation need not appreciably alter the relative distances between the centres of the polyhedral atoms as compared with the relative distances between the centres of the spheres from which they were derived. The argument is, of course, not altered if the deformed sphere represent the domain of paramount influence of a much smaller atom placed at its centre, instead of being completely filled with matter.

The problem now resolves itself into finding a homogeneous, close-packed arrangement of spheres of the appropriate volumes which shall satisfy the following conditions :—The whole assemblage, supposed indefinitely extended, must be partitionable into groups representing molecules; or, conversely, by taking clusters of spheres representing molecules it must be possible to pack the clusters closely so as to give a homogeneous assemblage. Moreover, the arrangement of three clusters about a fourth must be such that the central distances of any selected atom in the latter from the corresponding atoms in the former three clusters are compatible with the parameters of the crystal. Finally, the symmetry of the assemblage of spheres must be in accordance with the observed symmetry of the crystal. When all these conditions are satisfied, the assemblage may be looked upon as completely expressing the internal structure of the crystalline substance in question.

Examples of the Application of the Theory.[1]—The crystal structure of the elements must be based on close packed assemblages of equal spheres, since all the atoms of a given element are of the same dimensions. According to the theory the same will be true of binary compounds, although half the number of spheres refer to one element and half to the other, because in such compounds the valencies are equal. Now it has long been known that equal spheres lend themselves to packing of a very close kind. The spheres may be packed together closely in a layer (cf. the octahedron facet of Fig. 80), so that each sphere is in contact with six neighbours. Further,

[1] *Journ. Chem. Soc.*, 1907, **91**, 1150.

a second such layer can be superimposed so that its spheres rest in the cavities of the lower layer. Barlow has shown that there are two ways of placing a third layer upon these: either each sphere may be placed in a cavity so as to lie directly over a sphere in the first layer, or in such a cavity that this is not so. In the latter case an assemblage having cubic symmetry is obtained (Figs. 79 and 80), whilst in the former case the symmetry is that of the hexagonal system.

As a matter of fact, nearly all the elements and binary compounds crystallise in either the cubic or the hexagonal system. Out of the forty known crystalline forms of elements, twenty are cubic and fourteen hexagonal, and the numerical proportions are still higher in the halide salts of the alkalis, and the oxides and sulphides of the divalent metals. Moreover, in the hexagonal forms the parametral ratio $a : c$

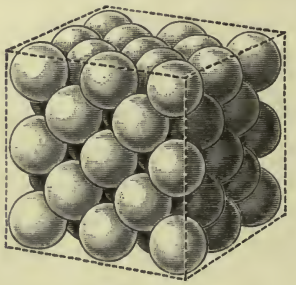


Fig 79.

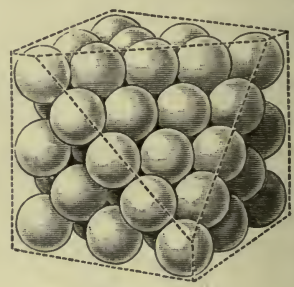


Fig 80.

corresponds in all cases very closely with the relative distances between corresponding sphere centres in the assemblage.

The greater portion of Barlow and Pope's work[1] refers to organic substances, the structures of which are more complicated than the simple assemblages just described. A great number of these substances, especially the hydrocarbons, are liquids at the ordinary temperature, but in the cases where the theoretical results can be tested, the arrangements deduced harmonise very closely with the crystal measurements. A notable feature of the work is the facile way in which the isomorphism of sodium nitrate and calcite, as well as the dimorphism of the latter substance, is interpreted.[2]

The Theory of Sollas.[3]—This theory differs radically from the

[1] *Journ. Chem. Soc.*, 1906, **89**, 1675; 1910, **97**, 2308.

[2] *Ibid.*, 1908, **93**, 1528.

[3] *Proc. Roy. Soc.*, 1898, **63**, 270, 286, 296; 1900, **67**, 493; 1902, **69**, 294; 1908, **80**, 267.

preceding in the volume relationships of the various atoms, the volumes of the spherical units being determined from the atomic volumes of each element in the substance concerned.

Sodium chloride presents a simple example of the method of attack used by Sollas. The atomic volumes of sodium and chlorine are supposed to be unequal, and the spheres representing these elements must be of different sizes. It is assumed that the unit of structure consists of four molecules packed together in such a way that every sodium atom comes above or below a chlorine atom (Fig. 81), whereby the inequality of the two

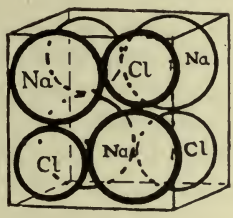


Fig. 81.

atomic volumes is compensated, the whole group attaining a cubic shape. By means of an ingenious train of reasoning from the known values of the atomic volume of sodium and of the molecular volume of the chloride, the conclusion is reached that the ratio of the diameters of the sodium and chlorine atoms is 2·272 : 2·490. The tetramolecular groups obviously correspond to Haüy's cleavage unit (p. 205), and they can be packed together indefinitely. The same structure holds for all the other halide salts of the alkalis, and by drawing them into the inquiry, the different values for the atomic volumes of halogen and alkali provide mutual confirmation.

In his latest memoir Sollas gives a complete study of anatase, rutile, and brookite—the three polymorphous forms of titanium dioxide, TiO_2. The ratio of the atomic volumes of titanium and oxygen is deduced to be 13·4 : 5·5, and the assemblages given are conspicuously in harmony with the facts.

There is an obvious difference[1] between the volume units of the atoms as employed by Sollas, and by Barlow and Pope, for in the former case the volumes of the atoms of two elements in the same compound are not simple multiples of each other, whilst in the latter case they are at any rate approximately so.

[1] For a comparison of the two theories, see Barker, *Journ. Chem. Soc.*, 1912, 101, 2492.

SYSTEMATIC DESCRIPTION OF THE METALS AND THEIR DERIVATIVES.

122 In the following systematic description of the metals, the latter are classified in groups according to the periodic system, each of these groups being further divided into two or more sub-groups. The members of each sub-group are described in the order of their atomic weight.

GROUP I.

Sub-group (*a*).—The Alkali Metals.

Lithium
Sodium
Potassium
Rubidium
Cæsium

Sub-group (*b*).—The Copper Group.

Copper
Silver
Gold

The metals of this group all form characteristic series of salts in which the metal is apparently monovalent, and except in the cases of copper and gold this series of salts is by far the most important. The division into sub-groups is more sharply defined than is usually the case, the metals copper, silver, and gold, which, as already pointed out, fall near the centre of the "double periods" (p. 52), showing only a limited resemblance to the alkali metals. The resemblance is most prominent in the case

of the two typical elements, lithium and sodium, the salts of which are frequently isomorphous with the corresponding silver salts. In the exact classification according to the periodic system, sodium belongs to the sub-group (*b*), for like copper, silver and gold it is a member of one of the "odd" periods; in its properties, however, it so closely resembles the metals of the sub-group (*a*) that it is always described together with these.

THE ALKALI METALS.

123 The above name is given to this group because the two most important members, sodium and potassium, are constituents of the substances which have been long known by the name of *alkalis*. The name alkali is first found in the works of the Latin Geber, and is the name there given to the soluble salt obtained by the lixiviation of the ashes of sea-plants. We find the same word employed to designate also the carbonate of potash obtained by a similar treatment of the ashes of land-plants. The difference between the alkalis potash and soda was at that time not understood, and in order to distinguish them from the carbonate of ammonia, the volatile alkali, they were both termed the fixed alkali. The distinction between the mild and caustic alkalis had long been known, and the mode of converting the former into the latter by boiling their solutions with lime was a well-recognised process. In the Historical Introduction (see Vol. I., p. 16) we have seen that Black, in the year 1755, was the first to explain this change, as he proved that the mild alkalis contain fixed air or carbon dioxide.

The first clear distinction between the two alkalis, potash and soda, appears to have been made by Duhamel in the year 1736, although Stahl pointed out that the alkali contained in common salt is different from that contained in wood-ashes, and this difference was indicated by the first being termed the mineral and the second the vegetable alkali. Marggraf showed in 1759 that the salts of the two alkalis possess totally distinct properties, and that whilst those of the common alkali tinge the flame of a spirit-lamp violet, those containing the base of common salt impart a yellow colour to the flame. It was, however, soon afterwards pointed out by Klaproth that the vegetable alkali potash was contained in several minerals, such as leucite,

and then the special name *potash* in English, *potasse* in French, and *kali* in German, was given to this particular alkali. Klaproth suggested for the mineral alkali the name *natron*, the English equivalent of which is *soda*, and the French *soude*. All these names had formerly been used indiscriminately for any alkali.

Up to the year 1807 the alkalis were considered to be simple substances. Lavoisier had indeed expressed a view that these bodies probably contained oxygen, owing to their analogy with other well-known metallic oxides, but Davy was the first to isolate the metals.

A few years later (1817), the lithium compounds were discovered by Arfvedson, and in 1860 the two remaining metals, rubidium and cæsium, were isolated by Bunsen and Kirchhoff.

The alkali metals are all soft silvery metals, which may be readily fused and volatilised, the melting and boiling points becoming lower with increasing atomic weight. The specific gravity increases with the atomic weight, but less rapidly than the latter, the atomic volume therefore becoming greater as we ascend the series. They are the most strongly electro-positive of the metals, their hydroxides being the most powerful bases known, and within the group itself the basicity increases with the atomic weight, that of cæsium hydroxide being the greatest.

The alkali metals form only one series of stable salts, and in these they are monovalent; a few halogen derivatives are known in which they have a valency of 3, 5, 7, or even 9, but these readily decompose into the free halogens and the monovalent halide compound of the metal. With very few exceptions the whole of the salts are soluble in water, those of lithium being the least soluble.

They combine with oxygen to form oxides of the general formula M_2O, which correspond to the stable salts; these are, however, as a rule difficult to prepare in the free state, since they combine very readily with oxygen forming higher oxides, and with water forming the characteristic hydroxides MOH, which are produced also by the direct action of the metals on water.

These metals all unite directly with hydrogen, forming crystalline hydrides, $(MH)_n$, which are decomposed by water.

LITHIUM, Li = 6·94.

124 Lithium was discovered in 1817 by Aug. Arfvedson whilst he was working in the laboratory of Berzelius.[1] He obtained a new alkali, and Berzelius gave to it the name *lithia*. It was first found in several minerals from the iron mines of Utö in Sweden, especially petalite and spodumene.

Lithium is derived from λίθεος, stony, as it was then believed to be an alkali whose presence was confined to mineral matter in contradistinction to the other alkalis which were found in vegetable and animal bodies. Since that time, however, lithium has been shown to be very generally distributed throughout the animal and vegetable kingdoms, this fact having been first ascertained by Bunsen and Kirchhoff in their earliest research on spectrum analysis in 1860 (p. 160).[2]

Sources of Lithium.—The most important minerals containing this element are *triphylite*, $(LiNa)_3PO_4 + (FeMn)_3(PO_4)_2$, or $(LiNa)(FeMn)PO_4$, containing from 1·6 to 3·7 per cent. of lithium; *petalite*, $LiAl(Si_2O_5)_2$, containing 2·7 to 3·7 per cent. of lithium; *lepidolite* or *lithia-mica*, 1·3 to 5·7 per cent.; *spodumene* or *triphane*, $LiAl(SiO_3)_2$, 3·8 to 5·6 per cent. Smaller quantities of lithium, whose presence can be ascertained by the spectroscope, are found in a large number of minerals. The water of certain mineral springs also contains large quantities of dissolved lithium salts. Thus Berzelius,[3] so long ago as 1822, detected this element in the water of Egger-Franzensbad, and in 1825 in the springs at Karlsbad and Marienbad. The spectroscope has since shown that lithium occurs in most mineral waters, in sea-water, and in that of almost every river[4] and surface spring. Some mineral springs contain lithium in considerable quantity. Thus Bunsen found 295·2 mgrm. of lithium chloride in one litre of the water of the Murspring at Baden-Baden,[5] and W. A. Miller[6] found 372 mgrm. in one litre of water from a spring in the Wheal Clifford mine at Redruth in Cornwall.

By the decomposition of rocks containing lithium this metal finds its way into the soil. It has been detected in that of the Limagne d'Auvergne, and can be traced in the ashes of the

[1] *Schweigger's Journal*, 1817, **22**, 93; *Ann. Chim. Phys.*, 1819, **10**, 82.
[2] *Phil. Mag.*, 1860 (4), **20**, 97. [3] *Pogg. Ann.*, 1825, **4**, 245.
[4] *On Thames Water.* A. and F. Dupré. *Phil. Mag.*, 1860 (4), **20**, 373.
[5] *Jahresb.*, 1861, 1091. [6] *Chem. News*, 1864, **10**, 181.

plants which grow in that district (Truchot).[1] It is widely distributed throughout the vegetable kingdom, occurring in the ash of the vine, in that of many cereals, in sea-weed and in tobacco (Bunsen and Kirchhoff). It has been found especially in the leaves of many plants, in cacao, coffee, and sugar-cane as well as in the residues from the extraction of beet-sugar.[2] It appears that lithium salts cannot replace potassium salts in plants; indeed, when added in quantity they generally seem to act as a poison. In certain plants, however, such as for instance the *Samolus Valerandi*, lithium appears to act beneficially, inasmuch as the stronger plants contain most lithium.

From the vegetable world lithium finds its way into the animal kingdom; thus Bunsen and Kirchhoff observed its presence in the ashes of milk and in human blood and muscular tissue.[3] Nor is lithium a metal which is confined to terrestrial matter, for Bunsen[4] detected it in two meteoric masses, one of which fell at Juvenas in France on May 15th, 1821, and the other at Parnallee in Southern India on February 28th, 1857, and Engelbach[5] found lithium in a meteorite from the Cape. The presence of lithium in the atmosphere of the sun is at present doubtful.

125 *Extraction of Lithium Salts.*—1. From petalite and lepidolite. The first method of extraction, proposed by Berzelius,[6] consists in fusing the powdered mineral with double its weight of lime. On dissolving the fused mass in hydrochloric acid, and evaporating with sulphuric acid, the lithium is obtained in solution as sulphate, together with some aluminium sulphate and gypsum. The first salt is precipitated by addition of chalk, and the second by ammonium oxalate. This method was improved by Regnault and again much simplified by Troost.[7] This latter chemist fuses the following mixture at a very high temperature in a wind furnace: finely powdered lepidolite, 10 parts; barium carbonate, 10 parts; barium sulphate, 5 parts; potassium sulphate, 3 parts. The heavy silicate and sulphate of barium sink to the bottom, and a layer of the sulphates of potassium and lithium is found at the top of the fused mass. These can be extracted by simple lixiviation. The sulphates are then con-

[1] *Ber.*, 1874, **7**, 653; *Compt. rend.*, 1874, **78**, 1022.

[2] Lippmann, *Ber.*, 1897, **30**, 3037. See also Tschermak, *Journ. Chem. Soc.*, 1900, Abstr., ii. 235.

[3] See also Hermann, *Pflüger's Archiv*, 1905, **109**, 26.

[4] *Annalen*, 1861, **120**, 253.

[5] *Pogg. Ann.*, 1862, **116**, 512.

[6] *Traité*, **2**, 89.

[7] *Compt. rend.*, 1856, **43**, 921.

verted into chlorides by the addition of barium chloride, the chlorides evaporated to dryness, and the lithium chloride extracted by treatment with a mixture of absolute alcohol and ether, or preferably, with pyridine.

An alternative method for the preparation of lithia from lepidolite, described by Schieffelin and Cappon,[1] is to decompose the finely powdered mineral with concentrated sulphuric acid by careful ignition at a temperature which is gradually raised from 120° to 340.° The mass is digested with water, the silica removed by filtration, and the aluminium sulphate converted into potash alum by the addition of potassium sulphate. A portion of the alum separates as crystals on standing, and the remainder is removed by the successive addition of calcium carbonate and freshly precipitated aluminium hydroxide; the last traces of aluminium are separated by the addition of calcium carbonate, the solution being made alkaline by means of slaked lime. The filtrate is then concentrated, the calcium salts precipitated as calcium oxalate, and traces of iron and manganese by potassium hypochlorite. The solution of lithium sulphate thus obtained is separated, and then converted into the carbonate by treatment with a slight excess of potassium carbonate solution.

2. For the purpose of extracting lithium salts from triphylite, a process proposed by Hugo Müller[2] is the best. This consists in dissolving the mineral in hydrochloric acid, oxidising with nitric acid, precipitating the phosphoric acid with a ferric salt, evaporating to dryness, and extracting with hot water. Chlorides of manganese and lithium are thus dissolved. The manganese is precipitated by sulphide of barium, and the excess of barium removed by sulphuric acid. The oxalate of lithium is obtained by evaporating with oxalic acid, and this on ignition is converted into the carbonate.

126 *Preparation of Lithium.*—The attempts made by Arfvedson and Gmelin to prepare metallic lithium were fruitless. They endeavoured to separate the metal by the electrolysis of its salts, but the battery they used was not powerful enough. Later on, the decomposition of lithia was tried by heating it with iron and carbon; these experiments also proved abortive. Then Davy succeeded in obtaining a small quantity of the metal by electrolysis, but was unable to examine its properties. In 1858 Bunsen and Matthiessen were the first to obtain lithium

[1] *J. Soc. Chem. Ind.*, 1908, **27**, 549. [2] *Annalen*, 1853, **85**, 251.

in quantity by electrolysis and to examine its properties carefully. The following is Bunsen's description of the process:[1] "Pure chloride of lithium is fused over a Berzelius' spirit-lamp (or Bunsen's gas lamp), in a small thick porcelain crucible and is decomposed by a zinc-carbon battery consisting of four to six cells. The positive pole is a small splinter of gas-coke, and the negative an iron wire about the thinness of a knitting-needle. After a few seconds, a small silver-white regulus is formed under the fused chloride round the iron wire and adhering to it, which after two or three minutes attains the size of a small pea: to obtain the metal the wire pole and the regulus are lifted out of the fused mass by a small flat spoon-shaped iron spatula. The wire can then be withdrawn from the still melted metal, which is protected from ignition by the chloride of lithium, with which it is coated. The metal may now be easily taken off the spatula with a pen-knife, after having been cooled under rock oil. As this operation can be repeated every three minutes, an ounce of chloride of lithium may be reduced in a very short time."

For the preparation of the metal on a somewhat larger scale it has been found advisable to employ a mixture of the chlorides of potassium and lithium in equal weights,[2] or preferably lithium bromide, to which 10—15 per cent. of the chloride has been added.[3] The metal can be obtained also by the electrolysis of solutions of the chloride in pyridine,[4] and in various alcohols.[5]

Lithium cannot be obtained in a similar manner to that by which sodium and potassium are prepared, viz., by heating the carbonate with charcoal, or the hydroxide with iron (Troost), but it distils over when pieces of magnesium are added to lithium hydroxide heated in an iron retort.[6]

Properties.—Lithium is a solid, possessing a silver-like lustre, but tarnishing on exposure to the air. It is much less oxidisable than potassium or sodium. It is not so soft as these metals, but is softer than lead, and makes a grey streak on paper. Lithium can be pressed into wire, and can be welded at ordinary tem-

[1] *Journ. Chem. Soc.*, 1856, 143.
[2] Guntz, *L'Electrochimie*, 1896, October.
[3] Ruff and Johannsen, *Zeit. Elektrochem.*, 1906, **12**, 186.
[4] Kahlenberg, *J. Physical Chem.*, 1899, **3**, 602.
[5] Patten and Mott, *J. Physical Chem.*, 1904, **8**, 153.
[6] Warren, *Chem. News*, 1896, **74**, 6.

peratures. It melts at 180° (Bunsen, Ruff, and Johannsen [1]), 179° (Masing and Tammann [2]), and if the melted metal be pressed between two sheets of glass, a surface is obtained which exhibits the colour and brilliancy of polished silver. Lithium floats on petroleum, and is the lightest of all known bodies which are solid at the ordinary temperature, its specific gravity varying from 0·5891 to 0·5983 (Bunsen).

Heated in the air lithium ignites at a temperature above its fusing point, burning tranquilly with a bright white light. It burns also when heated in hydrogen, chlorine, bromine, iodine, dry carbon dioxide, or sulphur vapour; it combines readily with nitrogen on heating, and slowly absorbs the gas even at the ordinary temperature, forming the nitride. When thrown on to water it oxidises, but does not fuse like sodium. Nitric acid acts on lithium so violently, that it fuses and often ignites. Sulphuric acid attacks it slowly, but dilute sulphuric and hydrochloric acids quickly. Silica, glass, and porcelain are attacked by lithium at a temperature below 200° (Bunsen and Matthiessen). Lithium is more electro-negative than sodium.

COMPOUNDS OF LITHIUM.

127 *Lithium Oxide*, Li_2O, *and Lithium Hydroxide*, LiOH.—Dry oxygen does not act upon lithium at the ordinary temperature. Indeed the metal may be melted in dry air without losing its brilliancy. Heated much above 180°, lithium takes fire and burns brilliantly in the air with the formation of lithium oxide, or lithia, which is coloured yellow by a small quantity of a higher oxide and volatilises slowly at 600°.[3] It may be prepared in a purer state by heating nitrate of lithium in a silver basin, and also by heating the hydroxide or carbonate in a current of dry hydrogen at 780°. It forms a white crystalline mass which dissolves slowly in water with the formation of a hydrated form of the hydroxide, LiOH. The anhydrous hydroxide can only be prepared from the hydrate, $LiOH,H_2O$, by heating the latter in a current of hydrogen below 140°. It forms a white, porous mass. The hydrate is

[1] *Zeit. Elektrochem.*, 1906, **12**, 186; Bernini, *Physikal. Zeit.*, 1905, **6**, 74.
[2] *Zeit. anorg. Chem.*, 1910, **67**, 183.
[3] Lebeau, *Compt. rend.*, 1903, **136**, 1256.

prepared by adding the calculated quantity of barium hydroxide to lithium sulphate and concentrating the resulting solution after filtering off the barium sulphate; crystals are thus obtained which are freed from water by heating to 33° in a current of pure hydrogen.[1] A second crystalline hydrate, $2LiOH,H_2O$, has also been obtained.[2]

Lithium Peroxide, Li_2O_2.—When hydrogen peroxide and alcohol are added to a solution of the hydroxide, the compound $Li_2O_2,H_2O_2,3H_2O$ is precipitated in hard, colourless crystals, which yield the anhydrous peroxide, Li_2O_2, when they are kept over phosphoric oxide.[3]

Lithium Hydride, LiH.—Lithium combines with hydrogen slowly at a dull red heat, and rapidly at a bright red heat with incandescence, forming the white solid hydride, which melts at 680°. It decomposes partially when slowly heated, and at 600° has a dissociation pressure of 27 mm. At a red heat the hydride burns in chlorine, yielding hydrogen chloride and lithium chloride, whilst with hydrogen chloride it forms the chloride and hydrogen (Guntz). It is only slowly altered in the air, and is decomposed by water with evolution of hydrogen and formation of the hydroxide.[4]

128 *Salts of Lithium.*—Many of the salts of lithium are isomorphous with those of sodium and silver, whilst in the alums this element can replace potassium and the other alkali metals. Lithium differs in a marked manner from sodium, potassium, &c., by forming a sparingly soluble carbonate and phosphate.

Lithium Chloride, LiCl.—This salt is formed when lithium burns in chlorine, or when lithia or the carbonate is dissolved in hydrochloric acid. Its preparation from spodumene and petalite has already been described. By evaporating the aqueous solution above 15·5°, or the alcoholic solution over sulphuric acid, the chloride is obtained in octahedra. The fused salt has a specific gravity of 2·068 at 25°, and melts at 606° (Ruff and Johannsen)[5] to a mobile liquid; it is one of the most deliquescent salts known, and is also very soluble in many of the alcohols and pyridine. When its aqueous solution is evaporated to dryness, traces of hydrochloric acid are given off, a little

[1] Dittmar, *J. Soc. Chem. Ind.*, 1888, **7**, 731; de Forcrand, *Compt. rend.*, 1907, **144**, 1321 and 1402.

[2] Muretow, *Ber.*, 1872, **5**, 331; Göttig, *Ber.*, 1887, **20**, 2912.

[3] de Forcrand, *Compt. rend.*, 1900, **130**, 1465.

[4] Guntz, *Compt. rend.*, 1896, **122**, 244; **123**, 694.

[5] *Zeit. Elektrochem.*, 1906, **12**, 186.

lithia being formed, and on redissolving, the liquid has an alkaline reaction. Three hydrated chlorides are known, viz., $LiCl,H_2O$, $LiCl,2H_2O$, and $2LiCl,3H_2O$.

One hundred parts of water dissolve:

At	0°	20°	65°	80°	140°	160°
LiCl	63·7	80·7	104·2	115	139	145 parts

The saturated solution boils at 171° (Kremers).

The chloride forms a series of unstable additive compounds with 1, 2, 3, and 4 molecules of ammonia.[1]

The product obtained by heating metallic lithium with lithium chloride in a current of hydrogen, which was previously regarded as a subchloride, has been shown by Guntz to be a mixture of the hydride and chloride.[2]

Lithium iodotetrachloride, $LiICl_4,4H_2O$, is obtained by the action of chlorine on a solution of lithium chloride and iodine in dilute hydrochloric acid, and crystallises in needles.[3]

Lithium sulphate, Li_2SO_4,H_2O, is obtained by dissolving the carbonate in dilute sulphuric acid, and crystallises in thin monoclinic plates which dissolve readily in water and alcohol. The *acid sulphate*, $LiHSO_4$, is also known.[4]

Lithium Nitride, Li_3N.—Lithium absorbs nitrogen at the ordinary temperature. The reaction takes place with incandescence when the metal is heated in a stream of the gas,[5] with formation of the nitride, Li_3N, which is, however, best prepared pure by heating the metal very gently in an iron dish in a slow stream of nitrogen.[6] It fuses at 840—845°, and attacks most substances when in the molten state.[7]

Lithiumamide, $LiNH_2$, is formed slowly by the prolonged action of liquid ammonia on metallic lithium at the ordinary temperature in a sealed tube.[8] It is obtained also by heating the nitride in either hydrogen or ammonia at temperatures between 340° and 480°.[9] The amide forms white, shining crystals which melt at 373—375° when heated in a sealed tube.

[1] Bonnefoi, *Ann. Chim. Phys.*, 1901 (7), **23**, 317.
[2] *Compt. rend.*, 1895, **121**, 945; *Ann. Chim. Phys.*, 1907, **10**, 15.
[3] Wells and Wheeler, *Zeit. anorg. Chem.*, 1891, **2**, 255.
[4] Schultz, *Pogg. Ann.*, 1868, **133**, 137.
[5] Deslandres, *Compt. rend.*, 1895, **121**, 886.
[6] Guntz, *Compt. rend.*, 1896, **123**, 995.
[7] Dafert and Miklauz, *Monatsh.*, 1910, **31**, 981.
[8] Ruff and Georges, *Ber.*, 1911, **44**, 502.
[9] Dafert and Miklauz, *Monatsh.*, 1912, **33**, 63.

Lithiumimide, Li_2NH, is obtained by heating lithiumamide from 360° to 450° in a silver dish, as a white, partially fused mass which is decomposed at 600°. On exposure to sunlight it is decomposed with the formation of the nitride and amide.[1]

Lithium azoimide, LiN_3, crystallises with $1H_2O$ in colourless hygroscopic needles and explodes between 115 and 298°.[2]

Lithium nitrate, $LiNO_3$, is prepared by dissolving the carbonate in nitric acid, and is very soluble in water and alcohol. It crystallises in anhydrous rhombohedra, isomorphous with sodium nitrate (Troost).

The solid salt in equilibrium with a saturated solution contains $3H_2O$ up to a temperature of 29·6° and a concentration of 57·5 per cent., $\frac{1}{2}H_2O$ from 29·6° to 61·1°, and above this temperature is the anhydrous salt.[3]

Normal Lithium Phosphate, Li_3PO_4, is distinguished from the phosphates of the other alkali metals by its slight solubility in water, in this respect resembling the phosphates of the next group of metals. It is precipitated as a crystalline powder by adding a lithium salt to common sodium phosphate together with caustic soda.[4] It may be obtained also by acting on lithium carbonate with phosphoric acid. It dissolves in 2,539 parts of water, and in 3,920 of water rendered alkaline by ammonia. In presence of ammonium salts it is much more soluble, and is precipitated from the solution by heating with caustic potash. It is readily soluble in hydrochloric and nitric acids; baryta water precipitates the phosphoric acid from the solution as barium phosphate, the whole of the lithium salt remaining in solution (W. Mayer). When a nitric acid solution of the normal salt is evaporated and the excess of free acid driven off, the di-hydrogen salt, LiH_2PO_4, remains behind. This is readily soluble, and on evaporation over sulphuric acid deposits deliquescent crystals.

Lithium carbide, Li_2C_2, is formed when a mixture of the carbonate with sugar charcoal is heated in the electric furnace,[5] and when metallic lithium is heated with carbon, or in a current of carbon monoxide or dioxide.[6] It is a transparent, colourless,

[1] *Ber.*, 1911, **44**, 502; *Monatsh.*, 1912, **33**, 63.

[2] Dennis and Benedict, *Zeit. anorg. Chem.*, 1898, **17**, 18; Curtius and Rissom, *J. pr. Chem.*, 1898 (2), **58**, 261.

[3] Donnan and Burt, *Journ. Chem. Soc.*, 1903, **83**, 335.

[4] Compare Quartaroli, *Gazz.*, 1907, **37** (i.), 598.

[5] Moissan, *Compt. rend.*, 1896, **122**, 362; 1898, **126**, 302.

[6] Guntz, *Compt. rend.*, 1896, **123**, 1273; 1898, **126**, 1866.

crystalline mass of sp. gr. 1·65 at 18°, and is a powerful reducing agent. It inflames in fluorine and chlorine at the ordinary temperature, and is readily attacked by bromine, iodine, oxygen, sulphur, phosphorus, and arsenic. Water decomposes it, forming lithium hydroxide and pure acetylene. It can be prepared also by acting on lithium dissolved in liquid ammonia with acetylene at −40° to −80°, and heating the crystalline compound $C_2Li_2,C_2H_2,2NH_3$ which is formed.[1]

When heated in nitrogen at 925° lithium carbide forms lithium cyanamide, along with some dicyanamide and cyanide; the absorption of the nitrogen is more rapid than in the case of calcium carbide.[2]

Normal Lithium Carbonate, Li_2CO_3.—This salt, unlike the carbonates of the other alkali metals, is but slightly soluble in water, thus more nearly resembling the carbonates of the next group of metals. It is precipitated as a crystalline powder when a concentrated solution of lithium chloride is poured into a solution of ammonium carbonate in aqueous ammonia, the mixture being heated so long as the precipitate increases in bulk.

The carbonate commences to decompose at about 600° into carbon dioxide and lithium oxide, which slowly volatilises;[3] when heated in a current of hydrogen at 780° the whole of the carbon dioxide is expelled.[4]

One hundred parts of water dissolve at:

0°	10°	20°	50°	75°	100°
1·539	1·406	1·329	1·181	0·866	0·728

parts of lithium carbonate, whilst at 102° the numbers 0·796 and 0·995 were obtained when the solution had boiled for 15 and 60 minutes respectively.[5] The solubility of the carbonate is increased by various sodium and potassium salts, and still more by ammonium salts.[6]

If the solution is slowly evaporated crystalline crusts or small transparent crystals of the salt separate out, and if these are suspended in water and carbon dioxide is passed in, *lithium hydrogen carbonate*, $LiHCO_3$, is formed. On evaporation the

[1] Moissan, *Compt. rend.*, 1898, **127**, 911.

[2] Tucker and Moody, *J. Amer. Chem. Soc.*, 1911, **33**, 1478.

[3] Lebeau, *Compt. rend.*, 1903, **136**, 1256.

[4] Dittmar, *J. Soc. Chem. Ind.*, 1888, **7**, 731; de Forcrand, *Compt. rend.*, 1907, **144**, 1402.

[5] Bewad, *J. Russ. Phys. Chem. Soc.*, 1884, i, 591.

[6] Geffcken, *Zeit. anorg. Chem.*, 1905, **43**, 197.

solution loses carbon dioxide, again depositing the normal salt. Lithium carbonate is employed in medicine, especially in gouty affections, since it acts as a solvent for uric acid.

Lithium Silicide, Li_6Si_2, is prepared by heating lithium and silicon together in a vacuum, and removing the excess of lithium by liquid ammonia or by heating to 500° *in vacuo*. It forms small lustrous crystals of a deep indigo blue colour, has the sp. gr. 1·12, and decomposes into its elements above 600°. This compound acts as a vigorous reducing agent, burns when heated in the air or oxygen, and is decomposed when heated in hydrogen and the halogens. Concentrated hydrochloric acid decomposes it, forming silicoethane, Si_2H_6, and water produces a violent reaction, the silicoethane, which is probably the first product, being decomposed by the lithium hydroxide also formed (Vol I., p. 900).[1]

Lithium orthosilicate, Li_4SiO_4, is prepared by fusing lithium carbonate with the requisite quantity of silica, and crystallises in the same form as olivin, whilst the *metasilicate*, Li_2SiO_3, has the same form as hypersthene. Both salts are partly decomposed by water. The *orthosilicate* melts at 1215° (Rieke and Endell[2]), the *metasilicate* at 1180° (Rieke and Endell[2]) or at 1202° (Jaeger[3]).

Detection and Estimation of Lithium

129 The presence of extremely small traces of lithium compounds ($\frac{9}{10000000}$ of a milligram) can be ascertained with certainty by means of the spectroscope. The luminous vapour of lithium, obtained by bringing a trace of a salt on a fine platinum wire into the non-luminous gas flame, gives, when examined by the spectroscope, two sharply defined lines—the one a very weak yellow line, Liβ (wave-length = 6104), the other a bright red line, Liα (wave-length = 6708). Not only do all the lithium salts when thus heated give this reaction, but ashes of plants and the lithium minerals only require for this purpose to be held in the flame. Natural silicates which contain only traces of lithium must first be subjected to the following treatment. A small portion of the substance is digested with hydrofluoric acid, and the residue moistened with

[1] Moissan, *Compt. rend.*, 1902, **134**, 1083.
[2] *Sprechsaal*, 1910, **43**, 683.
[3] *J. Washington Acad. Sc.*, 1911, **1**, 49.

sulphuric acid and heated; the dry mass is then treated with alcohol, and the extract allowed to evaporate in a shallow dish. The solid particles are scraped off and brought into the flame on the platinum wire (Bunsen).

Lithium is separated from all the heavy and earthy metals in the ordinary process of analysis. It may be separated from potassium by the precipitation of the latter metal as the insoluble double chloride of potassium and platinum, the corresponding lithium compound being soluble. It can be separated from sodium by the solubility of lithium chloride in a mixture of ether and absolute alcohol, but as by this process a small quantity of sodium chloride is found to be dissolved, it is best to determine the amount of chlorine in a given weight of the mixed chlorides, from which the quantities of lithium and sodium may be calculated. The best method for the separation of lithium chloride from the other alkali chlorides is to digest the solid chlorides repeatedly with pyridine, in which the lithium chloride only is soluble; the chloride is then recovered from the pyridine solution and converted into and weighed as lithium sulphate.[1]

The atomic weight of lithium was first accurately determined by Mallet in 1856 and 1859, and by K. Diehl in 1862. It was afterwards determined by Stas by converting the chloride into the nitrate, and by the determination of chlorine in lithium chloride, the atomic weight deduced from these numbers being 7·03. Richards and Willard[2] have since redetermined the atomic weight by converting the chloride into silver chloride, and obtained the value 6·94 (Ag = 107·88).

SODIUM. Na = 23·00

130 In the writings of the Old Testament (Jeremiah ii. 22) we find a substance used for washing purposes mentioned as *nether*. This same substance is mentioned in Proverbs as being one which effervesces when vinegar is poured over it, and in our version this substance is called nitre. In Luther's translation the name chalk is given to this body, but there can be little doubt that by the word *nether* was meant trona, or the native carbonate of soda, to which the names *νίτρον* in Greek and *nitrum* in Latin were applied.

[1] Kahlenberg and Krauskopf, *J. Amer. Chem. Soc.*, 1908, **30**, 1104.

[2] *J. Amer. Chem. Soc.*, 1910, **32**, 4.

At a later date the name *nitrum* was given to saltpetre; but up to the fourth century there is no doubt that nitrum signified the carbonate of soda originally obtained from the salt lakes in Egypt, to which the names *flos salis* and *spuma nitri* were given. Reasons for believing this are, amongst others, the facts stated by Pliny, that in the first place this nitrum does not decrepitate when thrown on the fire ("igni non exsilit nitrum") as saltpetre does; that, secondly, it possesses a fatty touch, this property being heightened by boiling it with lime; thirdly, that the nitrum is used both with and without oil in the baths ("in balneis utuntur (nitro) sine oleo"); and fourthly, that it is largely used in the manufacture of glass.

The word nitrum was, as we have already remarked, long applied indiscriminately to both soda and potash. The history of the distinction between these two bodies has also been dwelt upon. The terms soda and natron came into general use in the fifteenth century to distinguish fixed alkali from nitre.

131 The sodium compounds occur very abundantly and are universally diffused. Vast quantities of sodium chloride, NaCl, are found in extended deposits as rocksalt in different parts of the world and in various geological formations, whilst the same compound occurs in solution in sea-water, salt lakes, salt springs, and many mineral waters. The double fluoride of sodium and aluminium, or cryolite, $3NaF,AlF_3$, is found in large quantity in Greenland; sodium nitrate, or Chili saltpetre, $NaNO_3$, is deposited in beds several feet thick in the rainless districts of Southern Peru and Bolivia; the carbonate, Na_2CO_3, and the sulphate, Na_2SO_4, are found either in springs or as deposits in the beds of dried-up lakes. Many minerals, especially nepheline, sodalite, albite, labradorite, contain sodium silicate in considerable quantity, whilst traces of sodium compounds occur in all silicates. Indeed it is difficult to find any substance which does not contain traces of sodium as evidenced by the very delicate spectroscopic reaction.

Sodium compounds are found also in living organisms of all kinds. The whole of the animal body, especially the juices, is rich in sodium compounds, the carbonate, chloride, and phosphate chiefly occurring, together with sodium salts of organic acids.

Plants growing in or near the sea contain sulphate, iodide, and chloride of sodium. Sodium salts are, however, not characteristic of vegetable life in the same sense that potassium salts

are. Thus, whilst the latter alkali is always present in larger quantities in certain organs of the plant than in others, sodium appears in general to be equally diffused throughout the whole organism. It is also a remarkable fact that the sodium salts contained in the ashes of plants are insoluble in water, as they combine with the phosphates of the alkaline earths to form insoluble compounds. For this reason the presence of sodium compounds in the ashes of plants has often been overlooked.

Duhamel and Cadet have shown that if the plant *Salsola Soda*, which grows near the sea, and which yields an ash rich in soda salts, be transplanted to an inland situation, the ash gradually loses in soda and gains in potash, until at last the whole of the former disappears. On the other hand, if inland plants are grown near the sea the reverse change takes place (Correnwinder).

132 *Preparation of Metallic Sodium.*—Sodium, like potassium, was first obtained in 1807 by Davy [1] by electrolysis of caustic soda, though according to him it is less easily prepared in this way than potassium. Up to recent years sodium was manufactured by a process, proposed by Brunner, of igniting a mixture of sodium carbonate and charcoal, and this method was improved by Deville,[2] who showed that the manufacture of sodium is simpler and easier than that of potassium, as there is no liability to explosions. This process is, however, a costly and an uneconomical one, inasmuch as a considerable quantity of the sodium is volatilised and burns; some adheres to the receiver, and the reduction does not occur completely, so that in a well-conducted operation the sodium obtained is only about one-third of the theoretical yield, and, moreover, as it is necessary to expose the retorts to a white heat, they are rapidly burnt through and rendered useless. An improvement in this method of manufacture, introduced by Castner [3] in 1886, was the replacement of sodium carbonate by caustic soda. The reaction is expressed as follows:

$$6NaOH + 2C = 2Na_2CO_3 + 3H_2 + 2Na.$$

By this process, which was successfully worked for some time, the price of sodium was materially reduced, but subsequently Castner [4] introduced another method of manufacture, viz., the

[1] *Phil. Trans.*, 1808, **98**, 1. [2] *Ann. Chim. Phys.*, 1855 [3], **43**, 5.
[3] See Roscoe, *Proc. Roy. Inst.*, 1889, **12**, 453.
[4] *J. Soc. Chem. Ind.*, 1891, **10**, 777; Pat. No. 13,356 (1890).

electrolysis of caustic soda, which has placed the sodium industry on an entirely new basis, and obviated the great difficulties which necessarily beset all the older processes. The temperature of decomposition rises only a few degrees above 300°C., and thus the wear and tear of the apparatus is reduced to a minimum, whilst at the same time the whole of the sodium is obtained as metal. In the year 1807, Davy, with his battery of 100 cells, found it "impossible to produce the effects of decomposition on pieces of soda of more than fifteen or twenty grains in weight"; the process has now been so amended that at Weston Point, Runcorn, and at Newcastle-

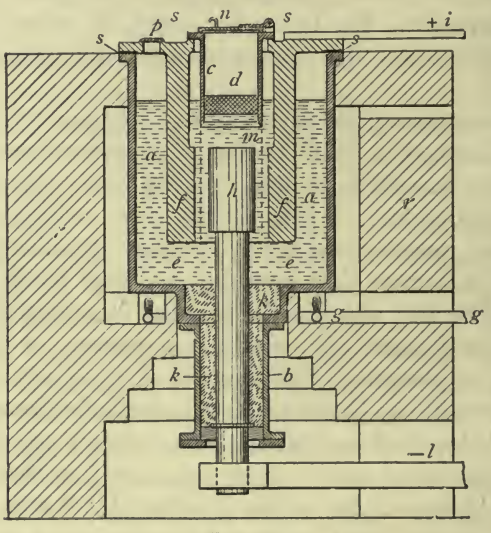


Fig. 82.

upon-Tyne, in England, by the Castner Kellner Alkali Company, at Rheinfelden in Germany by the Elektrochemische Fabrik Natrium, at Clavaux, France, by la Société d'Electrochimie, and in America by the Electrochemical Company of Niagara, no fewer than 4–5,000 tons of sodium are manufactured annually.

The apparatus consists of an iron vessel *a* (Fig. 82) suitably mounted in brickwork *r*, so that the heat applied by the gas burners *g* may be well distributed. The vessel *a* is provided with one or more base pipes *b* adapted to receive the negative electrodes *h*, which are preferably of metal and pass up into the vessel. Suspended directly above the cathode *h* is a tubular

iron receptacle *c* which is provided on its upper end with a lid *n*, whilst to its lower edges is secured an iron wire gauze *m*, which, when the receptacle *c* is placed in position, completely surrounds the cathode. The positive electrodes *f* are made of such metal as will withstand the oxidising action of the evolved gases, as, for instance, nickel, and either form part of the cover of the vessel *a* or are bolted to it, being so placed that when the cover is adjusted the electrodes are a suitable distance from, and directly surround, the gauze *m*. Electrical connection is made between the cover by the connection *i* with the positive pole of the dynamo, and with the negative pole by the connection *l*. The cover is provided with an opening *p* for the escape of the gases resulting from the electrolysis, this opening serving also for the introduction of a thermometer. Insulation is made at the points *ss*, by means of asbestos. The size and distance apart of the electrodes are both proportioned to the quantity of current to be supplied, the effective action of the apparatus being largely dependent on the accuracy with which this is carried out.

The sodium, being much lighter than the hydroxide, rises together with the hydrogen from the negative electrode and passes into the receiver *c*, the hydrogen escaping around the edges of the cover *n*, while the molten metal continues to collect in quantity. From time to time this collected metal *d* is removed by means of a large finely-perforated spoon, the perforations enabling the molten caustic to flow out whilst the metal remains in the spoon. Caustic is added to the bath from time to time to replace the metal removed, and in this way a continuous process may be carried on in an economical manner.

Any rise of temperature is followed by a proportionate loss of product and waste of electrical energy, but it is possible so to adjust the electrical current and the quantity of caustic alkali forming the electrolyte that the proper temperature will be maintained in a previously melted bath without external heat; or the current may be temporarily increased in order to melt the bath, being subsequently reduced, until the working temperature is attained; if large currents are used the bath and the electrodes may be artificially cooled by air or water circulation. The cathode may be conveniently sealed in the extension *b* by means of molten caustic *k* which is allowed to harden before beginning the process.

In order to secure a fair yield of metal for the current applied

it is necessary that the temperature of the electrolyte should not be allowed to rise above 330°, or 20° above the melting point of caustic soda.

The sodium thus obtained is sufficiently pure for ordinary purposes, and only requires to be remelted and then cast into sticks about one inch thick and a foot long. These may be preserved in closed vessels in dry air for a long time without undergoing any considerable oxidation, but it is usual first to moisten the sticks with petroleum. When in smaller masses it is advisable to keep the sodium under petroleum.

A process has also been proposed by Darling for the manufacture of sodium and nitric acid by the electrolysis of sodium nitrate, but has not yet found any extended application.

133 *Properties.*—Sodium is a white metal possessing a high silver-white lustre. It may be obtained in the crystalline condition by sealing up 100 grams of metal in a glass tube filled with hydrogen. The sodium is melted at one end of the glass tube and then allowed to filter through some wire gauze placed in a narrowed portion of the tube. The melted metal is thus rendered perfectly free from oxide, and must be fused in the clean part of the tube, allowed to cool partially, and then the central liquid portion suddenly poured off from the solidified crust. According to Long,[1] sodium crystallises in the tetragonal system, forming acute octahedra. The specific gravity of sodium at 0° was found by Davy to be 0·9348; later and more accurate determinations of Baumhauer give 0·9735 as its specific gravity at 13·5°. At −20° sodium is rather hard, at 0° it is very ductile, at the ordinary temperature it has the consistency of wax, at 50° it is semi-fluid, and it melts at 97·6°, forming a liquid resembling mercury in its appearance. Sodium boils at 877·5°,[2] emitting a vapour which is colourless when seen in thin layers, but of a peculiar purple colour by transmitted light when seen in quantity (Roscoe and Schuster), and which exhibits a green fluorescence.[3] With the exception of silver, copper, and gold, it conducts heat and electricity better than any of the metals (Matthiessen),

[1] *Journ. Chem. Soc.*, 1861, **13**, 123.

[2] Ruff and Johannsen, *Ber.*, 1905, **38**, 3601; compare Perman, *Journ. Chem. Soc.*, 1889, **55**, 328.

[3] Wiedemann and Schmidt, *Ann. Phys. Chem.*, 1896 [2], **57**, 447; Wood, *Phil. Mag.*, 1905 [6], **10**, 513; *Physikal. Zeitschr.*, 1906, **7**, 105; *Phil. Mag.*, 1906 [6], **12**, 499; 1909 [6], **18**, 530; Zickendraht, *Physikal. Zeitschr.*, 1908 **9**, 593; Dunoyer, *Compt. rend.*, 1911, **153**, 333; 1912, **154**, 815.

and next to cæsium, rubidium, and potassium, it is the most electro-positive metal (Bunsen).

Sodium has been obtained in the colloidal state by the electrical method (p. 73), forming an unstable violet-coloured solution in ethyl ether.[1]

When freely exposed to moist air sodium oxidises like potassium, although not quite so rapidly. It burns with a bright yellow flame when heated in the air, forming the monoxide and the dioxide. Thrown on to cold water it swims on the surface, disengaging hydrogen and dissolving, but not evolving heat enough to ignite the hydrogen. Brought into contact with hot water, or thrown on to a thick paste of starch, or wet filter paper, the evolved hydrogen ignites and burns with a yellow-tinted sodium flame.

Sodium is largely used for the manufacture of cyanides and sodium peroxide, and for the preparation of silicon, boron, and magnesium, and of certain organic substances such as artificial indigo and antipyrin. The greater part of the sodium now produced in England is sent to Glasgow, where it is converted into sodium cyanide by the Cassel Gold Extracting Company.[2] Sodium amalgam also has been employed in the process of extracting gold from the quartzose rock in which it occurs, and this amalgam, like sodium itself, is of great service as a reducing agent in the laboratory.

SODIUM COMPOUNDS.

Sodium and Oxygen.

134 Sodium forms two well-defined oxides, a strong basic monoxide Na_2O, and a peroxide Na_2O_2. In addition to these a grey suboxide possibly exists, and also a sesquioxide, Na_2O_3.

Sodium Suboxide, Na_3O, is stated to be formed when a clean surface of the metal is first exposed to air, and when pure air is passed through sodium just above its melting point. It is described as a grey arborescent mass, which burns when heated in the air, and decomposes water with evolution of hydrogen.[3]

[1] Svedberg, *Ber.*, 1905, **38**, 3616.

[2] Beilby, *Advances in Chemical Industry during the Nineteenth Century, Proc. Roy. Phil. Soc.*, Glasgow, 1904.

[3] de Forcrand, *Compt. rend.*, 1898, **127**, 364, 514.

Sodium Monoxide, Na_2O.—Sodium does not oxidise in perfectly dry air, but when heated in slightly moist oxygen it takes fire and burns with formation of a mixture of the monoxide and peroxide. If the amount of oxygen be limited and the sodium be not heated above 180°, only the former oxide is obtained,[1] and can be freed from the unaltered metal by distillation in a vacuum.[2]

The monoxide can be prepared also by heating sodium nitrate or nitrite with metallic sodium,[3] the nitrogen being liberated:

$$2NaNO_2 + 6Na = 4Na_2O + N_2.$$

It is a white, amorphous mass (Rengade), having a conchoidal fracture, and a sp. gr. of 2·805. It melts at a dull red heat, and undergoes volatilisation at a still higher temperature (Davy); when heated above 400° it is decomposed into the peroxide and metal, but in a vacuum is dissociated at 300°.[4] When brought in contact with water violent action occurs, sodium hydroxide being formed. Carbon dioxide is not absorbed by sodium monoxide when cold, but sodium carbonate is formed at 300°[1].

Sodium monoxide is the oxide corresponding to the monovalent sodium salts, to which class, as already stated, all the stable salts belong. They are characterised by the fact that almost all are readily soluble in water, even when the corresponding salts of the remaining alkali metals are sparingly soluble. The least soluble inorganic salt of sodium is the metantimonate.

Sodium Hydroxide, Sodium Hydrate, or *Caustic Soda*, NaOH.—When water is added to sodium monoxide great heat is evolved and the hydroxide is formed; it is obtained also when water is decomposed by sodium. It is best prepared in this way by placing metallic sodium in a pointed funnel of nickel gauze over water contained in a basin, and covering the funnel with a bell jar which stands in the basin, raised from the bottom by some pieces of glass rod. The water vapour attacks the sodium, and a solution of pure caustic soda (of about 40 per cent. strength) is formed, which drips into a platinum or nickel vessel placed under the funnel to receive it. The hydrogen evolved passes out through the water under the edge of the bell jar.[5]

[1] Holt and Sims, *Journ. Chem. Soc.*, 1894, **65**, 442.
[2] Rengade, *Compt. rend.*, 1906, **143**, 1152.
[3] German Patent, 142467 (22/7/1902).
[4] Rengade, *Compt. rend.*, 1907, **144**, 755.
[5] Küster, *Zeit. anorg. Chem.*, 1904, **41**, 474.

Care is needed in the construction of the apparatus for this preparation, as, if liquid water comes in contact with comparatively large pieces of sodium, dangerous explosions sometimes occur. The cause of these is not definitely known, but they are possibly due to the presence of carbide in the metal.[1]

The solution may be evaporated, and the caustic soda obtained in a fused state and cast into sticks. The hydroxide thus obtained is free from chloride and sulphate of sodium, and from alumina, silica, and oxide of iron.

In order to obtain it more cheaply a solution of sodium carbonate is boiled with milk of lime :

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3,$$

and it is now obtained also by the electrolysis of a solution of sodium chloride, the sodium first liberated reacting with the water to form caustic soda with evolution of hydrogen. The manufacture by both of these methods will be described later, together with that of sodium carbonate (p. 280).

Commercial caustic soda prepared by the first method always contains sodium chloride, sodium sulphate, alumina, and frequently silica and ferric oxide. It may be purified by dissolving in pure alcohol, and evaporating the clear solution to dryness in a silver basin (*Soude à l'alcool*, Berthollet). The product still contains traces of sodium chloride, carbonate and acetate, the latter being formed by the action of caustic soda on the alcohol.

Caustic soda is a white opaque solid, with a fibrous texture; it has a specific gravity of 2·13 (Filhol), melts at 310°, is rather less volatile than caustic potash, and decomposes into its elements at the melting point of cast iron; heated in an atmosphere of nitrogen at 400° it becomes quite anhydrous and shows no signs of decomposition when the temperature is raised to 720°.[2] It deliquesces in the air and when moist absorbs carbon dioxide, and acts as a powerful cautery. It is very soluble in water and in alcohol, one part dissolving in 0·47 part of the former, yielding a strongly alkaline solution. The fused substance rapidly corrodes most metals; cast iron and silver are slighted affected, gold being the only metal which is not attacked.

[1] Harpf and Fleissner, *Chem. Centr.*, 1906, II. 994; Küster, *ibid.*

[2] Bergmann, *Ber.*, 1909, **42**, 4728.

Hydrates of Caustic Soda.—The equilibrium curve for caustic soda and water is of a very complex character,[1] and indicates the existence of a number of hydrates. Among these the following have been isolated: $NaOH,H_2O$, melting at 64°, is always produced when a hot concentrated solution of the hydroxide is allowed to cool; $NaOH,2H_2O$, melting at about 12°, is obtained from 96·8 per cent. alcohol[2]; $2NaOH,7H_2O$ is deposited in large transparent tabular monoclinic crystals when a solution of soda-ley of specific gravity 1·365 is exposed to a temperature of −8°. These crystals melt at 6°, yielding a liquid having a specific gravity of 1·405 (Hermes),[3] but according to Pickering melt at 15·5°.

In addition to these there is evidence for the existence of two isomeric hydrates with $4H_2O$; $NaOH,5H_2O$; $NaOH,7H_2O$, and a complex labile hydrate with $3·11H_2O$. The hydrate $2NaOH,3H_2O$ has also been described.[4]

The following table gives the specific gravity of caustic soda solutions at 15°/4°, according to the experiments of Bousfield and Lowry:[5]

Percentage of NaOH.	Specific gravity.	Percentage of NaOH.	Specific gravity.
5	1·0555	30	1·3309
10	1·1111	35	1·3830
15	1·1665	40	1·4334
20	1·2218	45	1·4815
25	1·2768	50	1·5290

Caustic soda is a most useful substance, and is largely used for many industrial processes, its chief employment being in the manufacture of soap. A description of the methods used for its preparation on the large scale will be found in the sequel.

135 *Sodium Dioxide*, Na_2O_2, is formed when the metal is heated in an excess of air or oxygen, and is prepared on the large scale by placing sodium on aluminium trays, which are in turn placed on tram carriages which are passed through an iron tube heated to about 300°. The air is freed from moisture and carbonic acid before passing through the tube, and as the fully oxidised product is taken from the finishing end of the tube a fresh

[1] Pickering, *Journ. Chem. Soc.*, 1893, **63**, 890; Dietz, *Wissenschaft. Abhandl. Reichsanstalt*, 1900, **3**, 450.

[2] Göttig, *J. pr. Chem.*, 1889 (2), **2**, 360. [3] *Pogg. Ann.*, 1863, **119**, 170.

[4] de Forcrand, *Compt. rend.*, 1901, **133**, 223.

[5] *Phil. Trans.*, 1905, A. **204**, 253.

charge of sodium is placed at the other end, the tram carriages being pushed forward to admit the fresh trays. The finished product contains about 93 per cent. Na_2O_2. About 500 tons are manufactured per annum by this process by the Castner Kellner and other companies.

Pure sodium dioxide is yellow, but becomes white on exposure to the air from absorption of water and carbon dioxide.[1] It dissolves in water with partial formation of caustic soda and hydrogen dioxide, the latter decomposing on heating into water and oxygen, and an analogous decomposition takes place on addition of mineral acids, the corresponding sodium salt being formed. It does not give off oxygen, unless heated to very high temperatures, but acts as a very strong oxidising agent on any substance mixed with it, and is therefore used in the analysis of many minerals, such as iron pyrites, chrome ironstone, &c.; fused with finely divided gold, it forms sodium aurate.[2] It has a very violent action on glacial acetic acid, the whole mass becoming ignited, and in presence of moisture oxidises any readily combustible substances such as wood, paper, &c., and great care must therefore be exercised in dealing with large quantities of the dioxide. It is reduced to metallic sodium by charcoal, coke, or graphite at 300–400°.[3]

It absorbs carbon dioxide with formation of sodium carbonate and liberation of oxygen, and on account of this property its use has been proposed[4] for the regeneration of air in closed spaces contaminated by respiration, such as submarines, and in respiratory apparatus for use in atmospheres containing noxious gases. It also absorbs carbonic oxide with formation of sodium carbonate, and nitrous and nitric oxides with formation of sodium nitrate.[5] With ammonium persulphate it forms an explosive mixture.[6] When the solution in cold water is allowed to evaporate, large tabular hexagonal crystals of the hydrate $Na_2O_2,8H_2O$ separate out, which on standing over sulphuric acid lose water, forming the hydrate $Na_2O_2,2H_2O$. The first hydrate is formed also when alcohol is added to a mixed solution of caustic soda and hydrogen peroxide,[7] and

[1] Jaubert, *Compt. rend* , 1901, **132**, 35.
[2] Meyer, *Compt. rend.*, 1907, **145**, 805.
[3] Bamberger, *Ber.*, 1898, **31**, 451. [4] German Patent, 168717, 3/3/1904.
[5] Harcourt, *Journ. Chem. Soc.*, 1862, **14**, 276.
[6] Kempf and Oehler, *Ber.*, 1908, **41**, 2576.
[7] Fairley, *Journ. Chem. Soc.*, 1877, **31**, 125. See also de Forcrand, *Compt. rend.*, 1899, **129**, 1246 ; 1900, **130**, 1555.

these two hydrates are also formed when the peroxide is exposed to moist air free from carbon dioxide.[1] When carefully hydrated by means of ice it absorbs carbon dioxide at low temperatures with the formation of percarbonates.[2]

A colourless powder having the composition $Na_2O_2.2HCl$ is formed when sodium dioxide is suspended in carbon tetrachloride and treated with dry hydrochloric acid gas; this product is readily decomposed by water, yielding a solution of hydrogen peroxide.[3]

A solution of the dioxide in hydrochloric acid, consisting of sodium chloride and hydrogen dioxide, is now manufactured on the large scale, and is much used for bleaching straw.

Monosodium Hydrogen Peroxide, NaO.OH.—When sodium peroxide is treated with alcoholic hydrochloric acid or with absolute alcohol at 0°, the dioxide partially dissolves and a white powder remains which has the composition NaO_2H.[4] It dissolves in water at 0°, forming a strongly alkaline solution, which on warming decomposes into caustic soda and oxygen, the same decomposition taking place with explosion when the dry substance is heated. It does not yield salts with mineral acids, but with acetic acid forms a crystalline compound of sodium acetate containing hydrogen peroxide of crystallisation $2CH_3.COONa,H_2O_2$.[5] Its formation from the dioxide is represented by the equation:

$$Na_2O_2 + C_2H_5OH = NaOC_2H_5 + NaO.OH.$$

Monosodium hydrogen peroxide gives off oxygen on addition of potassium permanganate, evolves chlorine with hydrochloric acid, and liberates iodine from potassium iodide at the ordinary temperature.

The dry substance is not acted upon by carbon dioxide, but in presence of a trace of moisture it is decomposed by the gas; an aqueous solution absorbs carbon dioxide at low temperatures forming an unstable percarbonate.[6] When treated with absolute alcohol or with hydrogen peroxide, a stable peroxide is formed containing hydrogen peroxide of crystallisation, $2NaHO_2,H_2O_2$;[7]

[1] Jaubert, *Compt. rend.*, 1901, **132**, 86.
[2] Wolffenstein and Peltner, *Ber.*, 1908, **41**, 280; German Patent, 188569.
[3] Jaubert, German Patent, 229572. [4] Tafel, *Ber.*, 1894, **27**, 816, 2297.
[5] D'Ans and Friederich, *Zeit. anorg. Chem.*, 1912, **73**, 325.
[6] Wolffenstein and Peltner, *loc. cit.*
[7] D'Ans and Friederich, *loc. cit.*

the same substance is formed by treating sodium ethoxide with a mixture of 30 per cent. hydrogen peroxide and absolute alcohol,[1] and by the action of an ethereal solution of anhydrous 100 per cent. hydrogen peroxide on metallic sodium.[2]

Sodium Trioxide, Na_2O_3, is formed according to Joannis,[3] by the action of an excess of oxygen on a solution of sodium in liquid ammonia. It is decomposed by water with evolution of oxygen and formation of the hydrated dioxide, and by carbon dioxide with evolution of oxygen.

Sodium and Hydrogen

136 *Sodium Hydride*, NaH.—When sodium is heated in hydrogen at 370°, the hydride is produced as a colourless crystalline sublimate. It has the specific gravity 0·92, and is insoluble in organic solvents and in liquid ammonia, but dissolves in fused sodium. When strongly heated in a vacuum it dissociates into its elements. The hydride is at once decomposed by water with formation of caustic soda and hydrogen, burns when heated in dry air, and ignites spontaneously in moist air. It burns brilliantly in fluorine, chlorine, and nitrogen peroxide, and is decomposed by hydrogen chloride, nitric and sulphuric acids, and by solid oxidising agents.[4] When the hydride is heated in carbon dioxide, carbon is liberated, whilst it combines with moist carbon dioxide to form sodium formate,[5] $H.CO_2Na$. The absorption of hydrogen by sodium was observed by Troost and Hautefeuille,[6] but they did not obtain the crystalline hydride. The heat of formation of the solid compound from its elements is 16·6 cal.[7]

Sodium and the Halogens.

137 *Sodium Fluoride*, NaF, is prepared by neutralising aqueous hydrofluoric acid with caustic soda or sodium carbonate.

[1] Wolffenstein and Peltner, *loc. cit.*; *German Patent*, 196369.

[2] D'Ans and Friederich, *loc. cit.*

[3] *Compt. rend.*, 1893, **116**, 1370; *Ann. Chim. Phys.*, 1906, (8) **7**, 5.

[4] Moissan, *Compt. rend.*, 1901, **133**, 803; 1902, **134**, 71; Holt, *Proc. Chem. Soc.*, 1903, 187; *Mem. Manch. Phil. Soc.*, 1909, **53** (xvii.), 1.

[5] Moissan, *Compt. rend.*, 1903, **136**, 723.

[6] *Ann. Chim. Phys.*, 1874 (5) **2**, 273.

[7] de Forcrand, *Compt. rend.*, 1905, **140**, 990; compare also Keyes, *J. Amer. Chem. Soc.*, 1912, **34**, 779.

It crystallises in cubes and sometimes in octahedra,[1] has a specific gravity of 2·766, and melts at 980° (Ruff and Plato). It is sparingly soluble in water, 100 parts of water dissolving 4 parts of the salt at 15° (Frémy). It is sometimes employed as an antiseptic.

Sodium Chloride, or Common Salt, NaCl.—Davy states that sodium takes fire when brought into chlorine gas. Wanklyn[2] has, however, shown that dry chlorine does not attack sodium even in the melted state. Probably Davy's chlorine was moist. Metallic sodium also retains its brightness in liquid chlorine at −80°.

Chloride of sodium occurs as rock-salt in large deposits in various geological strata, in solution in sea-water and brine springs, and in small quantities in all running water. The chief European deposits of salt occur in the trias formation. The most important in England are those at Northwich and Winsford in Cheshire, at Fleetwood in Lancashire, and at Middlesboro' in Yorkshire. On the Continent important deposits occur at Weilizca in Galicia, at Reichenhall, Hallein, Berchtesgaden, and other localities in the Tyrol, and at Stassfurt in the north of Germany. Rock-salt occurs also in France, Spain, and Switzerland, and in Asia, Africa and America, in various localities.

The Cheshire salt-beds occur in the keuper (triassic) beds. They are two in number, separated by about thirty feet of clay: they are together about sixty yards thick, and extend over an area of sixteen miles by ten.

The methods adopted for raising and working the salt differ widely, according to the nature of the deposit and its situation. Sometimes the rock-salt is mined and brought up to the surface; generally, however, salt springs or brine wells are artificially constructed by sinking a bore-hole through the overlying strata to the salt-bed, and allowing water to pass down this boring. The water soon becomes saturated with salt, and it is then pumped up and the salt obtained by evaporation, either by means of fuel or by exposure to air.

Owing to the presence of cheap fuel and water carriage the quantity of salt raised in England is much larger than that obtained in any other country. About 1,658,000 tons of salt were obtained from English brine in the year 1905, and in

[1] Körbs, *Zeit. Kryst. Min.*, 1907, **43**, 451.
[2] *Chem. News*, 1869, **20**, 271.

addition 231,000 tons were raised as rock-salt; the total production in 1910 was 2,051,000 tons.

The process of evaporating the brine, 100 parts by weight of which in Cheshire usually contain 23·3 parts of salt, is of the simplest kind. Indeed it has not been improved since the time of the Romans, and although very numerous patents for the purpose have been taken out, no economy in fuel has been effected. The brine is evaporated in large shallow iron pans heated by means of fires placed beneath. The appearance and quality of the salt deposited depends upon the temperature at which the brine is kept and the rapidity with which the process of evaporation is conducted. The Cheshire brine contains about 1·65 per cent. of calcium sulphate, $CaSO_4$, and about 0·05 per cent. of magnesium chloride, $MgCl_2$. The first of these salts is deposited as pan-scale when the brine is boiled down.

In Germany, where fuel is dear, the brine is sometimes evaporated by exposing it to the action of the air by a process termed "graduation." After having been allowed to trickle several times over high walls of fagots and thus become more concentrated, it is boiled down in pans.

Preparation of Salt from Sea-water.—The evaporation of sea-water in salterns, or brine-pans, by the aid of air and the sun's heat has been carried out from very early times. In England, at Hayling Island near Portsmouth, and at Lymington, and in Scotland at Saltcoats on the Ayrshire coast, such salterns have been in use quite recently.

In countries more favoured by sunshine, such as the coast of France, Sicily, Portugal, and Spain, these salterns are more numerous than with us. When this salt, termed Bay-salt, is deposited, a mother-liquor called Bittern is left. This consists of the chlorides, sulphates, and bromides of magnesium and potassium, and from this bromine is obtained.

All common salt contains a small quantity of sodium sulphate, calcium sulphate, and magnesium chloride. The presence of the last compound renders the salt liable to become damp in the air. This same substance not infrequently attacks the iron pans, causing the presence of traces of ferric chloride in the salt.

In order to prepare chemically pure sodium chloride from common salt, hydrochloric acid gas is passed into a saturated solution of salt. A precipitate of the pure chloride is thrown

down, the alkali sulphates and magnesium chloride remaining in solution. The precipitate is transferred to a filter, washed with concentrated hydrochloric acid, and then dried and fused in a platinum basin.

Properties.—Sodium chloride crystallises in cubes. Rock-salt is usually found in cubical crystals, sometimes, however, in octahedra and intermediate forms. It possesses an agreeable saline taste and a specific gravity at 0° of 2·16. Rock-salt is highly diathermanous, that is, it permits the heat rays, dark as well as visible, to pass through it; hence it is a valuable substance in thermal researches. Sodium chloride melts at 815·4° (Meyer, Riddle and Lamb), 808° (Amadori),[1] and begins to volatilise at temperatures not far removed from its melting point; hence it cannot be fused without loss (Stas). It boils at 1750° (Emich).[2] A colloidal form of sodium chloride has been prepared by Paal.[3]

When heated with silicic or boric acid, sodium chloride is decomposed, with liberation of hydrochloric acid and formation of a silicate or borate. It has been proposed to utilise the former of these reactions for the manufacture of sodium carbonate, but without practical success. Sulphuric acid decomposes it, hydrochloric acid and hydrogen sodium sulphate or the normal sulphate being formed.

According to the experiments of Berkeley,[4] one hundred parts of water dissolve the following quantities of sodium chloride at the corresponding temperatures:

Temp.	0°	10°	20°	30°	40°	60°	80°	100°	107·7°
NaCl.	35·74	35·78	35·94	36·16	36·47	37·19	38·02	39·12	39·65

Hence sodium chloride is not, as was formerly supposed to be the case, equally soluble in cold and in hot water. The boiling point of the saturated solution is 107·7° at 745 mm. pressure (Berkeley). The specific gravity of salt solutions of different strengths is, according to Gerlach,[5] as follows:

Percentage of NaCl.	5	10	15	20	25
Specific Gravity at 15°.	1·03624	1·07335	1·11146	1·15107	1·19228

Chloride of sodium is nearly insoluble in absolute alcohol.

[1] *Atti R. Accad. Lincei*, 1912 [v.], **21**, i. 467.
[2] *Verh. Ges. deut. Naturforsch. Aerzte*, 1910, ii. 65.
[3] *Ber.*, 1906, **39**, 1436, 2859; Paal and Kuhn, *Ber.*, 1908, **41**, 51.
[4] *Phil. Trans.*, 1904, A. **203**, 206.
[5] *Zeit. anal. Chem.*, 1869, **8**, 279.

When the temperature of a saturated solution of sodium chloride is lowered to $-10°$, a crystalline hydrate separates out[1] having the composition $NaCl,2H_2O$; this is obtained also by cooling a solution of sodium chloride in hot hydrochloric acid, in which it is sparingly soluble.[2] When brine is further cooled to $-22°$, acicular bundles of crystals separate out. These consist of the cryohydrate, which contains 23·7 per cent. of sodium chloride (Guthrie).[3]

Sodium chloride is frequently found as rock-salt in blue crystals, which become colourless when heated. A similar coloration can be produced by exposing colourless crystals to the vapour of metallic sodium or potassium, to the cathode rays, and to the radiation from radium. The artificial coloration appears to be due either to the presence of the metal or a subchloride, but it has not yet been definitely ascertained whether the natural coloration is due to the same cause or to the presence of an organic colouring matter.[4]

Sodium Bromide, NaBr, and *Sodium Iodide*, NaI, are prepared by processes similar to those employed in the case of the corresponding potassium salts, the latter being more largely used (p. 331). Both crystallise from hot concentrated solution in anhydrous cubes, whilst if the solutions be allowed to evaporate at the ordinary temperature, monoclinic prisms are deposited. These contain two molecules of water of crystallisation, $NaBr,2H_2O$ and $NaI,2H_2O$, and are isomorphous with the corresponding hydrate of sodium chloride; hydrates with $5H_2O$ also exist at low temperatures. The bromide melts at 748°, and the iodide at 662° (Amadori).[5] Both sodium bromide and sodium iodide have been prepared in a colloidal form by Paal.[6]

Sodium Hypochlorite, NaClO, may be prepared by passing chlorine over powdered sodium carbonate slightly moistened with water; it is, however, usually obtained in solution on the small scale by passing chlorine into a solution of caustic soda, which yields a mixture of the chloride and hypochlorite:

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

[1] Lowitz, *Crell. Ann.*, 1793, i. 314.

[2] Bevan, *Chem. News*, 1877, **35**, 17.

[3] *Phil. Mag.*, 1875, (4), **49**, 9; Matignon, *Compt. rend.*, 1909, **148**, 550.

[4] See Wöhler and Kasarnowski, *Zeit. anorg. Chem.*, 1905, **47**, 353, where the various possibilities are discussed and references to the literature given; and Siedentopf, *Physikalische Zeitschr.*, 1905, **6**, 855.

[5] *Atti R. Accad. Lincei*, 1912 [v.], **21**, i. 467.

[6] *Ber.*, 1906, **39**, 2859; Paal and Kühn, *Ber.*, 1908, **41**, 51.

Traces of iron render these solutions unstable, but in the absence of iron fairly stable solutions, yielding about 30 per cent. of available chlorine, can be prepared. When more concentrated solutions are cooled they deposit solid sodium hypochlorite in fine needles belonging to the tetragonal system, which contain 39·9 per cent. of NaClO, 54·7 per cent. of water, and small amounts of sodium chloride, chlorate, and hydrate. These crystals are much more stable than the solutions from which they crystallise.[1]

Technical Preparation.—Sodium hypochlorite in solution was known about 1790, and in 1820 it was well known as Eau de Labarraque, and subsequently as Eau de Javelle indiscriminately with the potassium hypochlorite solution. The solution was first made by passing chlorine into a soda solution, but afterwards by decomposing bleaching powder by a soda solution or by sodium sulphate; these solutions have been made in large quantities in South Lancashire and France for bleaching purposes; they contain 7 to 15 per cent. available chlorine.

Still weaker solutions are now prepared in large quantities at a large number of paper and bleaching works by electrolysing a solution of common salt under suitable conditions so that the hypochlorite shall not be converted into chlorate, nor yet reduced by the escaping hydrogen to chloride. The solutions are therefore made only weak, seldom exceeding 1 per cent. available chlorine, but as they are manufactured where used, this is no disadvantage. The first practical process was that of Hermite in 1884, since when numerous variations have been introduced; a full account of these has been given by Engelhardt,[2] and the theoretical considerations underlying the process have been described by Abel.[3] The solutions frequently contain hypochlorous acid. Probably 10,000 horse-power is used in the various installations.

The crystals prepared by Muspratt and Smith in their first experiments melted at about 20° C. and then rapidly decomposed, so that there was little prospect of making this material technically useful; but in 1903 Muspratt succeeded in drying the crystals in a vacuum, and obtained a powder melting

[1] Muspratt and Shrapnell-Smith, *J. Soc. Chem. Ind.*, 1898, **17**, 1096; 1899, **18**, 210.

[2] *Hypochlorite und elektrische Bleiche*, 1903. See also Allmand, *Applied Electrochemistry*, 1912, p. 318; and Kershaw, *J. Soc. Chem. Ind.*, 1912, **31**, 54.

[3] *Hypochlorite und elektrische Bleiche*, 1905.

about 45° C. and containing from 40 to 60 per cent. available chlorine.

Sodium Chlorate, $NaClO_3$.—This salt is obtained, according to Muspratt and Eschelmann's process, by saturating milk of magnesia with chlorine and adding sodium carbonate to the resulting solution of magnesium chloride and chlorate. The liquor, after filtering from precipitated carbonate, is boiled down, the sodium chloride fished out as it separates, and the sodium chlorate purified by recrystallisation. In Pechiney's process the solution of calcium chlorate and chloride obtained by passing chlorine into hot milk of lime is evaporated down and as much as possible of the calcium chloride removed by crystallisation, the liquid being then decomposed with salt-cake:

$$CaCl_2 + Ca(ClO_3)_2 + 2Na_2SO_4 = 2CaSO_4 + 2NaCl + 2NaClO_3.$$

According to the process of Best[1] it is manufactured also by acting with chlorine on a solution of sodium carbonate or bicarbonate at temperatures not exceeding 35°, the reaction being probably:

$$3Na_2CO_3 + 3Cl_2 = NaClO_3 + 5NaCl + 3CO_2.$$

It is also prepared by the electrolysis of the chloride in a similar manner to the potassium salt.

Sodium chlorate is dimorphous, crystallising in combinations of the cube and tetrahedron showing also tetartohedral faces (Class 28, p. 201), or in rhombohedral forms of the hexagonal system. It has a sp. gr. of 2·29, and becomes damp when kept exposed to air. It is much more soluble in water than the potassium salt, 100 parts of water dissolving according to Kremers:

At	0°	20°	40°	60°	80°	100°	120°
Parts of $NaClO_3$	81·9	99	123·5	147·1	175·6	232·6	333·3.

It dissolves readily also in warm alcohol.

Sodium chlorate melts at 302° (Carnelley), 248° (Retgers), and is then for the most part converted into sodium chloride and perchlorate, with evolution of only a small quantity of oxygen (Schlössing). It is used chiefly in the manufacture of aniline black, its greater solubility making it more suitable for this purpose than the potassium salt.

[1] *J. Soc. Chem. Ind.*, 1895, **14**, 865. See also Grossmann, *J. Soc. Chem. Ind.*, 1896, **15**, 158.

Sodium Perchlorate, $NaClO_4$, is prepared by heating the chlorate or by neutralising perchloric acid with soda. It is very soluble in water, from which it crystallises at the ordinary temperature in long pointed plates containing one molecule of water, and at 50° in anhydrous rectangular prisms.[1] It occurs in small quantities in Chili saltpetre.

Sodium and Sulphur.

138 *Sodium Sulphides.*—These compounds are prepared in a similar manner to the corresponding potassium salts (p. 337), which they closely resemble. The monosulphide, Na_2S, crystallises with $9H_2O$ at ordinary temperatures; hydrates with $6H_2O$ and with $5\frac{1}{2}H_2O$ are formed from solutions above 48.°[2] The hydrosulphide, NaHS, crystallises with $2H_2O$ and $3H_2O$, and is also obtained as an anhydrous powder by heating the sulphide at 310° in a current of hydrogen sulphide.[3] The only crystalline polysulphide which has been obtained has the formula $Na_4S_9{,}14H_2O$, although there is evidence that lower polysulphides are formed by the direct union of sodium or sodium sulphide with sulphur.[4]

The sulphides Na_2S and Na_2S_5 have been obtained also by the action of sulphur on a solution of sodium in liquid ammonia, and the selenides, Na_2Se, Na_2Se_4, and tellurides, Na_2Te, Na_2Te_3, are formed in a similar manner.[5] Sodium sulphide is prepared on the large scale, and used in the manufacture of soluble soda-glass.

Sodium Hyposulphite, $Na_2S_2O_4$.—This salt, the formation and preparation of which have already been discussed (Vol. I., p. 448),[6] is used by the dyer and calico printer as a reducing agent for indigo, and is also employed in the laboratory for the purpose of estimating free oxygen or the quantity of that element contained in substances from which it is readily

[1] Potilitzin, *J. Russ. Phys. Chem. Soc.*, 1889, i. 258.

[2] Parravano and Fornaini, *Atti. R. Accad. Lincei*, 1907 (v.), **16**, ii. 464.

[3] German Patent, 194881.

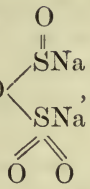
[4] Bloxam, *Journ. Chem. Soc.*, 1900, **67**, 761; Locke and Austell, *Amer. Chem. J.*, 1898, **20**, 592; Blanksma, *Proc. K. Akad. Wetensch. Amsterdam*, 1901, **3**, 457.

[5] Hugot, *Compt. rend.*, 1899, **129**, 299, 388.

[6] See also *Bull. Soc. Ind. Mulhouse*, 1904, **74**, 348; *Ber.*, 1905, **38**, 1048; Jellinek, *Zeit. anory. Chem.*, 1911, **70**, 93.

evolved. It has been obtained also by the direct action of sulphur dioxide on sodium hydride[1] according to the equation :

$$2NaH + 2SO_2 = Na_2S_2O_4 + H_2.$$

According to Binz[2] and to Reinking, Dehnel, and Labhardt,[3] this salt has the constitutional formula  , which represents it as an anhydro-salt of sulphurous acid, $H{\cdot}SO_2{\cdot}OH$, and of the hypothetical sulphoxylic acid, $H{\cdot}SO{\cdot}OH$. This constitution is confirmed by its behaviour to organic reagents.[4]

Normal Sodium Sulphite, Na_2SO_3.—The anhydrous salt is obtained as a crystalline precipitate by heating a cold saturated solution of the hydrated salt, and remains unaltered in the air. The hydrate $Na_2SO_3,7H_2O$ is prepared by saturating a solution of a known quantity of sodium carbonate with sulphur dioxide, and then adding the same quantity of sodium carbonate. The crystals which are deposited are transparent monoclinic prisms, which lose the whole of their water at 150°. The anhydrous salt crystallises in short hexagonal prisms.[5] The solution has an alkaline reaction and sharp taste. Crystals of the hydrate $Na_2SO_3,10H_2O$ are obtained, according to Muspratt, by allowing the aqueous solution to evaporate over sulphuric acid.

The solubility of the anhydrous salt is almost independent of the temperature; 100 parts of water dissolve 28·01 parts at 37° and 28·26 parts at 84°. The solubility of the hydrate $Na_2SO_3,7H_2O$ is as follows :—100 parts of water dissolve[5]—

	At	2°	10·6°	18·2°	29°	37·2°
Parts of Na_2SO_3		14·82	20·01	25·31	34·99	44·08

The transition temperature of the two modifications is about 22°.[5]

Sodium sulphite is used as an "antichlor" to remove any

[1] Moissan, *Compt. rend.*, 1902, **135**, 647.
[2] *Zeit. Farb. u. Textil. Chem.*, **4**, 161. [3] *Ber.*, 1905, **38**, 1075.
[4] *Ber.*, 1906, **39**, 3317.
[5] Hartley and Barrett, *Journ. Chem. Soc.*, 1909, **95**, 1178.

excess of chlorine from fabrics which have been bleached with chloride of lime, and sometimes also as an antiseptic.

Sodium Hydrogen Sulphite, $NaHSO_3$.—If a solution of sodium carbonate is saturated with sulphur dioxide whilst cold, this salt separates out in cloudy crystals, and alcohol precipitates it from aqueous solution as a white powder. It has an acid reaction, smells of sulphurous acid, and has an unpleasant sulphurous taste. A saturated solution of this salt is a commercial article, and is used by brewers for sterilising their casks, etc.

Sodium Disulphite or *Sodium Metabisulphite*, $Na_2S_2O_5$, or $Na{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}Na$, is obtained by supersaturating a soda solution with sulphur dioxide, and may be prepared on the large scale by passing sulphur dioxide into dry monohydrated sodium carbonate, Na_2CO_3,H_2O.[1] It is a white crystalline soluble salt, which gradually evolves sulphur dioxide in the air and is converted into sodium sulphate.

139 *Normal Sodium Sulphate*, Na_2SO_4.—This compound is commonly known in the anhydrous state by the commercial name of *Salt-cake*, whilst the hydrate, $Na_2SO_4,10H_2O$, is called Glauber's salt. We find the first mention of this salt in Glauber's work, *De naturâ salium*, published in 1658. He obtained it as the residue left in the preparation of hydrochloric acid by the action of oil of vitriol upon common salt, and believed this simple aperient to be possessed of most valuable medicinal properties, whence it came to be known as *Sal mirabile Glauberi*.

The salt occurs native in the anhydrous condition as thénardite, and in solution in sea-water and in the water of salt-lakes, as well as in large quantities in certain mineral springs. Thus the water at Friedrichshall contains large quantities of the salt, which since 1767 has been obtained by evaporation and used in medicine as *Sal aperitivum Fridericianum*. A native compound of sodium sulphate with calcium sulphate, $Na_2SO_4,CaSO_4$, termed *glauberite*, is also found in several localities.

Sodium sulphate is prepared on an enormous scale as salt-cake, the first step in the manufacture of carbonate of soda by the Leblanc process, about 360,000 tons of salt-cake being annually produced at present (see p. 288). For this purpose common salt is decomposed either by sulphuric acid or by the

[1] Carey and Hurter, *Patent* 4512, Nov. 1882; *J. Soc. Chem. Ind.*, 1883, 2, 349.

combined action of sulphur dioxide, air, and aqueous vapour. The details of these processes will be described under the head of the alkali manufacture.

Sulphate of sodium is also obtained as a residue in many chemical operations, especially in the preparation of nitric acid from Chili saltpetre in the sulphuric acid manufacture.

If ordinary Glauber's salt is allowed to remain exposed to the air, or more quickly if heated, the anhydrous salt is obtained; and if a solution of Glauber's salt saturated at about 35° is slightly heated, rhombic crystals of the anhydrous salt separate out. These are identical in form with crystals of thénardite, and isomorphous with those of silver sulphate, Ag_2SO_4. It has a specific gravity of 2·655, melts at 883°,[1] possesses a saline bitter taste, has a neutral reaction, and does not dissolve in alcohol. When heated on charcoal before the blowpipe in the reducing flame, sodium sulphide is formed.

One hundred parts of water dissolve the following quantities of the salt calculated as anhydrous sodium sulphate (Mulder[2]).—

At	0°	10°	20°	30°	34°	40°
Na_2SO_4	5·02	9·00	19·40	40·00	55·00	48·8

At	50°	60°	70°	80°	90°	100°	103·5
Na_2SO_4	46·7	45·3	44·4	43·7	43·1	42·5	42·2

The saturated solution boils at 103·5° (Mulder), 101·9° (Berkeley). The abnormal solubility of this salt has already been discussed (p. 113).

Hydrated Sodium Sulphate.—The decahydrate, $Na_2SO_4,10H_2O$, commonly known as Glauber's salt, crystallises from aqueous solution at the ordinary temperature in large colourless monoclinic prisms, which are isomorphous with chromate and selenate of sodium. These crystals effloresce on exposure to dry air, melt in their water of crystallisation at 32·48°, and lose the whole of it below 100°.

The Hepta-hydrated Salt, $Na_2SO_4,7H_2O$, is deposited in hard, clear, rhombic crystals when a supersaturated solution of the decahydrate is allowed to cool below 12°, or when such a solution is covered with a layer of warm alcohol of specific gravity 0·835.[3]

[1] Nacken, *Chem. Centr.*, 1908, i. 1850.

[2] Compare Berkeley, *Phil. Trans.*, 1904, A. **203**, 209.

[3] Compare Hartley, Jones and Hutchinson, *Journ. Chem. Soc.*, 1908, **93**, 825; Gernez, *Compt. rend.*, 1909, **149**, 77; Smits and Wuite, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 244.

Sodium Hydrogen Sulphate, $NaHSO_4$.—This salt, commonly known as bisulphate of soda, is obtained in large triclinic prisms when equivalent quantities of sodium sulphate and sulphuric acid are dissolved in water and the solution evaporated at a temperature above 50°. Like the corresponding potassium salt it is decomposed by alcohol at once into sulphuric acid and the normal salt. A hydrated salt, $NaHSO_4,H_2O$, is also known, as well as a salt of the formula $Na_3H(SO_4)_2$, which crystallises in lustrous needles.[1]

Sodium Disulphate, $Na_2S_2O_7$, is formed by heating sulphur trioxide together with common salt (Rosenstiel):—

$$2NaCl + 3SO_3 = Na_2S_2O_7 + SO_2Cl_2.$$

The same compound is formed by the gentle ignition of sodium hydrogen sulphate. When more strongly heated, it yields sulphur trioxide and normal sulphate.

Sodium Thiosulphate, $Na_2S_2O_3$.—This salt, discovered in 1799 by Chaussier, and still commonly known by its old name of hyposulphite of soda, is prepared on the large scale for use as an antichlor in the paper manufacture, and as a solvent for the unaltered silver bromide in photography. It is obtained by boiling sulphur with soda-lye, and passing sulphur dioxide into the yellow solution until it is colourless, or by boiling sodium sulphite with sulphur. A cheaper process is to decompose the soluble calcium thiosulphate obtained by the oxidation of alkali waste, either by means of sodium carbonate or sodium sulphate. The solution of sodium thiosulphate is drawn off from the carbonate or sulphate of calcium and evaporated down in iron pans. Anhydrous sodium thiosulphate is obtained by passing oxygen or air over anhydrous sodium sulphide at 100°–150°.[2]

Sodium thiosulphate forms large transparent prisms belonging to the monoclinic system, which contain $5H_2O$. The salt is odourless, possesses a cooling taste, and does not exhibit an alkaline reaction, nor does it undergo alteration in the air. The crystals melt in their own water at 48·5°, and when heated to 215° all the water is driven off, whilst at 220° they decompose with separation of sulphur (Pape). The salt has a specific gravity of 1·672, is very soluble in water, in which it readily forms supersaturated solutions, but does not dissolve in alcohol.

Sodium thiosulphate forms a large number of hydrates, and the

[1] D'Ans, *Ber.*, 1906, **39**, 1534. [2] German Patent, 194882.

equilibrium curve of this substance and water is very complex.[1] The ordinary pentahydrate is stable in contact with water at all temperatures up to 48·2°; from this point to 65° the dihydrate is stable, and above 70° the anhydrous salt. Isomeric hydrates with $5H_2O$ and $2H_2O$ also exist as well as hydrates with $6H_2O$, $4H_2O$, $1\frac{1}{2}H_2O$, $4/3H_2O$, $1H_2O$ (3 isomerides), and $\frac{1}{2}H_2O$.

The aqueous solution cannot be preserved for any length of time without decomposition, as it very slowly deposits sulphur and is partially converted into sulphite. Sodium thiosulphate is represented by the formula[2] $SO_2\begin{cases}ONa\\SNa\end{cases}$. When treated with sodium amalgam it yields sodium sulphite and sodium sulphide:—

$$Na_2S_2O_3+2Na=Na_2SO_3+Na_2S.$$

It is acted upon by iodine in aqueous solution at the ordinary temperature with formation of sodium tetrathionate:—

$$2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6,$$

and is largely employed in volumetric analysis in association with the estimation of iodine. Ferric salts also convert it into tetrathionate.[3]

Sodium and Nitrogen.

140 *Sodamide*, $NaNH_2$.—This compound, discovered by Gay-Lussac and Thénard, is prepared by passing dry ammonia gas over sodium heated to 300–400° in an iron retort, and forms a waxy mass of crystalline structure, which is white when pure but frequently has a greenish or olive-brown colour.[4] It softens at 149° and melts at 155°, and at a temperature of 500–600° slowly decomposes into its elements, but does not, as stated by Gay-Lussac and Thénard,[5] yield a nitride of the formula Na_3N. When heated in a current of carbon dioxide sodamide glows with formation of caustic soda and cyanamide, and on warming

[1] Taylor, *Proc. Roy. Soc., Edin.*, 1898, **22**, 248; Young and Mitchell, *J. Amer. Chem. Soc.*, 1904, **26**, 1389, 1413; Young and Burke, *J. Amer. Chem. Soc.*, 1906, **28**, 315; Dawson and Jackson, *Journ. Chem. Soc.*, 1907, **91**, 552; Jones, *ibid.*, 1909, **95**, 1672.

[2] Compare Vol. I. p. 455; also Price and Twiss, *Journ. Chem. Soc.*, 1907, **91**, 2024.

[3] Hewitt and Mann, *Journ. Chem. Soc.*, 1913, **103**, 324.

[4] Titherley, *Journ. Chem. Soc.*, 1894, **65**, 504.

[5] See, however, Zehnder, *Ann. Phys. Chem.*, 1894, **52**, 56.

with nitrous oxide it is converted into sodium azoimide (Vol. I., p. 519).

Sodium Azoimide, NaN_3, forms hexagonal crystals and is readily soluble in water. It can be kept molten for some hours without decomposition.[1]

Sodium Nitrite, $NaNO_2$, is formed when the nitrate is heated, and is usually manufactured either by the electrical oxidation of atmospheric nitrogen (Vol. I., p. 547), or by heating sodium nitrate with lead, or with charcoal or sulphur in presence of caustic soda.[2] To obtain the pure salt, silver nitrite is treated with the equivalent amount of a solution of sodium chloride, or nitrous fumes from nitric acid and starch or arsenious acid are passed into a solution of caustic soda or sodium carbonate.[3] The salt is faintly yellow, melts at 271°, and yields a yellow solution in water, which is faintly alkaline to litmus (Divers), but according to Boguski the pure dry salt is colourless.[4] It crystallises in oblique four-sided prisms or transparent rhombohedra, and is somewhat hygroscopic; at 15°, 100 parts of water dissolve 83·3 of the salt. It is largely used in the preparation of the coal-tar colours.

141 *Sodium Nitrate*, $NaNO_3$.—This salt, commonly known as cubic saltpetre or Chili saltpetre, is of special historical interest, as it was by the examination of differences in crystalline form exhibited by this compound and ordinary nitre that the distinction between the alkalis potash and soda was first observed by Bohn in 1683. Boyle, somewhat later, noticed that cubic saltpetre was formed in the preparation of aqua regia from common salt and nitric acid, and Stahl first pointed out the distinct character of the alkali-basis of common salt, and fully described the preparation of cubic saltpetre.

Sodium nitrate occurs in nature, as a wide-spread deposit known as "Caliche" in the rainless districts of Tarapaca, Peru, Northern Chili, and Bolivia.[5] In these beds it is associated with common salt, gypsum, sodium sulphate, and smaller quantities of sodium iodate, chlorate and perchlorate, the crude material containing from 27 to 65 per cent. of the pure salt. This is purified by solution and crystallisation. After refining, the salt

[1] Curtius and Rissom, *J. pr. Chem.*, 1898 (2), **58**, 261; Dennis and Benedict, *Zeit. anorg. Chem.*, 1898, **17**, 18.

[2] See Morgan, *J. Soc. Chem. Ind.*, 1908, **27**, 483.

[3] Divers, *Journ. Chem. Soc.*, 1899, **75**, 86.

[4] *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 543.

[5] See Bryce's *South America*, pp. 42, 208.

contains about 97·7 per cent. of pure nitrate, 1·84 of sodium chloride, 0·35 of sodium sulphate, and 0·11 of water.[1]

The best mode of separating the last 2 per cent. of sodium chloride is to add to the boiling and saturated solution one-tenth of its weight of nitric acid, stir it until cool, and collect the precipitated nitrate, which may then be washed by a dilute acid and afterwards dried.

Sodium nitrate crystallises in obtuse rhombohedra,[2] whose interfacial terminal edge angle is 106° 36′ (Fig. 83), and is therefore isogonous with calc-spar.

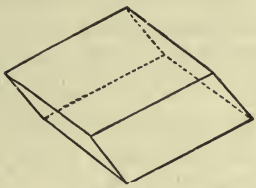


Fig. 83.

The specific gravity of the salt is 2·26. It melts without decomposition at 316–318° (Carnelley), and when ignited undergoes decomposition with evolution of oxygen, nitrogen, and nitrous fumes. It is very soluble in water and deliquesces when exposed to moist air. One hundred parts of water dissolve:[3]

At	0°	10°	20°	40°	60°	80°	100°	119°
Parts	73	80·5	88	104·9	124·6	148	175·5	208·8

The solution containing 58·5 of the salt to 100 of water solidifies at −18·5°, and the saturated solution boils at 119°.

This salt dissolves also in dilute alcohol. One hundred parts of spirit, containing 61·4 per cent. of alcohol, dissolve at 26° 21·2 parts of sodium nitrate. It does not deflagrate so violently as nitre with charcoal or other inflammable bodies, but it has sometimes been used for making blasting and other powders which are not required to fire quickly.

Sodium nitrate is used in considerable quantities for the manufacture of nitric acid and also of sulphuric acid, but much the largest quantity is employed as a manure, since it readily yields up its nitrogen to plants growing in soil where it is present. This salt and ammonium sulphate are by far the most important sources of nitrogenous manure. In 1860 the output of the crude nitrate from South America was over 60,000

[1] Compare Newton, *J. Soc. Chem. Ind.*, 1900, **19**, 408.

[2] Sénarmont, *Compt. rend.*, 1854, **38**, 105; Barlow and Pope, *Journ. Chem. Soc.*, 1908, **93**, 1538.

[3] Berkeley, *Phil. Trans.*, 1904, A. **203**, 211; Miers and Isaac, *Journ. Chem. Soc.*, 1906, **89**, 428.

tons, and has greatly increased since that date, being about 764,000 tons in 1888, and 2,500,000 tons in 1912.

Sodium and Phosphorus.

142 *Sodium Phosphide*, Na_3P.—Sodium dissolved in liquid ammonia reacts with red phosphorus to form a red compound, $Na_3H_3P_2$, which loses phosphine when heated and is decomposed by water and acids with evolution of phosphine.[1] Phosphine also reacts with sodium in presence of liquid ammonia forming the compound, NaH_2P, which is converted by heat into the phosphide, Na_3P. This is decomposed by water yielding phosphine.[2] An unstable phosphide, Na_2P_5, is formed when sodium and phosphorus are heated together in a vacuum at 450° for several days.[3]

Sodium Hypophosphite, NaH_2PO_2,H_2O.—This salt is obtained by adding sodium carbonate to a solution of calcium hypophosphite, and allowing the solution to evaporate in a vacuum. Pearly tabular crystals are deposited, which deliquesce on exposure to the air, and are readily soluble in absolute alcohol. It is now employed in medicine for the same purposes as phosphorus.

Sodium Orthophosphates.—As orthophosphoric is a tribasic acid, three sodium salts exist in which one, two, or three atoms of the hydrogen in the acid are replaced by metal:—

(1) Trisodium or normal sodium orthophosphate, Na_3PO_4, $12H_2O$.

(2) Hydrogen disodium orthophosphate, $Na_2HPO_4,12H_2O$.

(3) Dihydrogen sodium orthophosphate, $NaH_2PO_4,4H_2O$.

These all give yellow precipitates of trisilver phosphate, Ag_3PO_4, when their solutions are brought into contact with silver nitrate. (Vol. I., p. 662.)

Normal Sodium Orthophosphate, Na_3PO_4.—This salt, first described by Thomson[4] as phospho-carbonate of soda, is prepared by adding in the form of caustic soda at least half as much sodium as it already contains to a solution of the next salt, common sodium phosphate, and evaporating to the point of crystallisation. The hydrated salt crystallises out, the mother-

[1] Hugot, *Compt. rend.*, 1895, **121**, 206; 1898, **126**, 1719.
[2] Joannis, *Compt. rend.*, 1894, **119**, 557.
[3] Hackspill and Bossuet, *Compt. rend.*, 1912, **154**, 209.
Ann. Phil., 1825, **26**, 381.

liquor retaining the excess of caustic soda. The crystals freed from the liquor are rapidly dissolved in twice their weight of hot water, the liquid filtered, and then left to crystallise (Graham). The anhydrous salt may be obtained by fusing common sodium phosphate or pyrophosphate with an excess of sodium carbonate. The pyrophosphate is not altered by boiling with caustic soda (Graham).

The crystals, containing $12H_2O$, form thin six-sided prisms, which do not change on exposure to air, and have a specific gravity of 1·618. They melt at 73·3°, and at 100° lose all but one molecule of water, which is given off at a red heat. 100 parts of water at 15·5° dissolve 19·6 parts of the hydrated salt (Graham), and the solution is strongly alkaline to litmus. A hydrate with $7H_2O$ has also been described.[1]

Di-sodium Hydrogen Orthophosphate, Na_2HPO_4.—This salt is the common phosphate of soda, which was first prepared from urine, and described in 1740 by Haupt under the name of *sal mirabile perlatum*. It was afterwards obtained by neutralising phosphoric acid with soda, and in 1787 was introduced as a medicine by Pearson. It occurs in the blood of animals, and especially in the urine of the carnivora. It is best prepared from bone phosphoric acid by adding sodium carbonate so long as effervescence occurs. The precipitated phosphates of calcium and magnesium are then filtered off, and the liquid is boiled down and allowed to crystallise. The large transparent crystals obtained are monoclinic prisms containing $12H_2O$. They have a specific gravity of 1·525, melt at 36·45° (Shiomi), and are isomorphous with the corresponding sodium hydrogen arsenate $Na_2HAsO_4,12H_2O$. Exposed to air, the crystals effloresce, but do not lose their form.

The following is the solubility of the anhydrous salt in 100 parts of water:

At	10·26°	25·15°	40·29°	60·23°	99·77°
Na_2HPO_4	3·55	12·02	54·88	83·00	102·15

There are three breaks in the solubility curve, at 36·45°, 48° and 95·2° respectively; the first corresponds with the transition from the hydrate with $12H_2O$ to one with $7H_2O$, the second with that from the latter to a hydrate with $2H_2O$, and the third with the charge from the dihydrate to the anhydrous salt. The dihydrate is obtained by fusing the dodecahydrate in its water

[1] Hall, *Journ. Chem. Soc.*, 1887, **51**, 97.

of crystallisation and evaporating the resulting solution at 70·75°; the anhydrous salt is similarly obtained at a temperature of about 99·5°.[1] The saturated solution boils at 105°.

This salt is insoluble in alcohol; it possesses a cooling saline taste, and turns red litmus solution blue. The solution is usually faintly alkaline to phenolphthaleïn; this alkalinity is ascribed by Geissler[2] to the presence of sodium carbonate, whereas according to Brunner[3] it is a property of the pure salt.

Common sodium phosphate is used as a mild purgative. The commercial salt frequently contains sodium sulphate as an impurity, which can be removed by recrystallising the phosphate from hot water.

Di-hydrogen Sodium Phosphate, NaH_2PO_4.—To prepare this salt phosphoric acid is added to a solution of common sodium phosphate, until the mixture no longer precipitates barium chloride. It is then evaporated to a small bulk, and allowed to stand for some days to crystallise (Mitscherlich). This salt is dimorphous, two kinds of large transparent crystals separating out, containing one molecule of water; according to Mitscherlich, both are forms of the rhombic system, but according to Joly and Dufet, one of the varieties is monoclinic.[4] Hydrates with $2H_2O$ and $4H_2O$ are also known.[5]

The crystals have an acid reaction, and a specific gravity of 2·04. They lose all their water of crystallisation at 100°, and at 204° lose the elements of water (Graham) with formation of acid pyrophosphate:

$$2NaH_2PO_4 = Na_2H_2P_2O_7 + H_2O.$$

At 240° they give off the whole of their water and form monometaphosphate:

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

Di-hydrogen sodium phosphate is very soluble in water, but not in alcohol. The solution is acid to litmus and phenolphthaleïn, but neutral to methyl orange.

Various double salts, such as $NaH_5(PO_4)_2$[6] and $Na_3H_3(PO_4)_2$,[7] are also known.

[1] Shiomi, *Mem. Koll. Sci. Eng. Kyōto*, 1908, **1**, 406; Kitawaki, *ibid.*, 1909–10, **2**, 237.

[2] *Zeit. anal. Chem.*, 1898, **37**, 323.

[3] *Ibid.*, 1898, **37**, 740.

[4] *Compt. rend.*, 1886, **102**, 1391.

[5] Imadsu, *Mem. Koll. Sci. Eng. Kyōto*, 1912, **3**, 257.

[6] Giran, *Compt. rend.*, 1902, **134**, 711.

[7] Senderens, *Compt. rend.*, 1902, **134**, 713.

Sodium Pyrophosphates.—These salts are tetrabasic, and give with silver nitrate a white precipitate of silver pyrophospate, $Ag_4P_2O_7$; they do not coagulate albumen, and their solutions when boiled with an acid yield the salts of the tribasic ortho-acid.

Normal Sodium Pyrophosphate, $Na_4P_2O_7,10H_2O$.—This salt is obtained in the anhydrous state as a colourless glassy mass by igniting common sodium phosphate. When it is dissolved in water, and the solution evaporated, crystals of the deca-hydrate are deposited in monoclinic prisms. The solution has an alkaline reaction. It is not converted into the ortho-salt by boiling alone, but this conversion takes place rapidly on addition of an acid, even acetic, to the boiling solution (Stromeyer). When gently heated, or exposed over sulphuric acid in a vacuum, it loses all its water. 100 parts of water dissolve the deca-hydrate as follows:

At 0°	10°	20°	30°	40°	50°	60°	80°	100°
5·41	6·81	10·92	18·11	24·97	33·25	44·07	63·40	93·11

Di-hydrogen Sodium Pyrophosphate, $Na_2H_2P_2O_7$.—This salt is prepared by heating common sodium phosphate to 150° with strong hydrochloric acid, or by heating sodium di-hydrogen phosphate to a temperature of 190–204°, as already explained. It may be prepared also by dissolving the normal pyrophosphate in acetic acid, and precipitating the solution with alcohol; it is thus obtained as a white crystalline powder, which dissolves readily in water, the solution having an acid reaction.

Sodium Metaphosphates.—These salts, which were first discovered by Graham (Vol. I., p. 665), exist in a large number of modifications, which all have the empirical formula, $NaPO_3$, but their molecular formula is probably in most cases some multiple of this. Great uncertainty exists as to the true molecular weights of the various salts.

Sodium Hexametaphosphate, $(NaPO_3)_6$, the most important of these salts, often called deliquescent, vitreous, or Graham's metaphosphate, is prepared by heating to complete fusion either sodium di-hydrogen phosphate, microcosmic salt,[1] or acid sodium pyrophosphate (v. Knorre), and also in a similar manner from all the other metaphosphates. The melted mass must be quickly cooled, to avoid the formation of the trimetaphosphate.

[1] Graham, *Phil. Trans.*, 1833.

The product is a vitreous mass, which dissolves in water and alcohol, the solutions having a slightly acid reaction.

The same salt appears to be formed by the action of sodium sulphide solution on the lead metaphosphate prepared by heating lead oxide with phosphoric acid and fusing the resulting salt at a temperature above 400° (Fleitmann's tetrametaphosphate).[1]

The solution gradually decomposes with formation of acid sodium pyrophosphate.

When treated with ammonium chloride it yields a salt having the formula $Na(NH_4)_5(PO_3)_6$, and hence is probably a hexametaphosphate. According to Tammann,[2] it is a mixture of at least two isomeric hexametaphosphates.

Insoluble Sodium Metaphosphate, ($NaPO_3$) —This salt, whose molecular weight is unknown, but which is usually termed the *monometaphosphate*, is obtained by heating microcosmic salt at 335°, or sodium nitrate with a slight excess of syrupy phosphoric acid. It is a white powder almost insoluble in water, but soluble in dilute acids, which is converted by boiling caustic soda solution into sodium orthophosphate.[3]

Sodium Dimetaphosphate, $(NaPO_3)_2,2H_2O$ (Fleitmann).—This is prepared by the action of a boiling solution of sodium sulphide on copper dimetaphosphate, which is obtained by heating a mixture of phosphoric acid with a copper salt or copper oxide, at a temperature not exceeding 448°. It dissolves in 7·2 parts of water, and crystallises in slender needles. It has a strong tendency to form double salts.[4]

According to Tammann, it has the molecular formula $(NaPO_3)_3$, whereas Warschauer,[5] from the determination of the equivalent conductivity at different concentrations, concludes that this salt is in reality a tetrametaphosphate, the hydrated salt having the formula $(NaPO_3)_4,4H_2O$.

Sodium Trimetaphosphate, $(NaPO_3)_3,6H_2O$.—Some doubt also exists as to the true molecular formula of this salt. From a study of the normal salts which can be prepared from it, such as $NaCa(PO_3)_3$, Fleitmann attributed to it the formula given above, but Tammann [6] was led by the determination of the

[1] Warschauer, *Zeit. anorg. Chem.*, 1903, **36**, 188.

[2] *J. pr. Chem.*, 1892 (2), **45**, 467.

[3] Maddrell, *Journ. Chem. Soc.*, 1851, 373.

[4] *Pogg. Ann.*, 1849, **78**, 246; Glatzel, *Diss. Würzburg*, 1880; quoted by v. Knorre, *Zeit. anorg. Chem.*, 1900, **24**, 369.

[5] *Zeit. anorg. Chem.*, 1903, **36**, 165.

[6] *Zeit. physikal. Chem.*, 1890, **6**, 122; *J. pr. Chem.*, 1892 (2), **45**, 417.

freezing point and electrical conductivity of a series of solutions to formulate it as the dimetaphosphate, Fleitmann's dimetaphosphate being considered on similar grounds as the trimetaphosphate. v. Knorre[1] and Wiesler,[2] on the other hand, decide for the original formula from the determination of the equivalent conductivity at various concentrations.

It is formed when microcosmic salt is exposed to a moderate heat (Graham), and when the fused hexametaphosphate is allowed to cool slowly.[3]

It is best prepared pure by heating ordinary sodium phosphate with one-third of its weight of ammonium nitrate for six hours at 300° and recrystallising the product (v. Knorre).

The cold solution in water is permanent, and neutral both to methyl orange and phenolphthaleïn, but when boiled it gradually becomes acid with formation of sodium di-hydrogen phosphate.

In addition to these a large number of other metaphosphates have been described, namely, tetra-, penta-, octo-, deca-, and tetrakaideca-metaphosphates, having the general formulæ:

$$(M'PO_3)_4,\ (M'PO_3)_5,\ (M'PO_3)_8,\ (M'PO_3)_{10},\ \text{and}\ (M'PO_3)_{14}.$$

Sodium and Arsenic.

143 *Sodium Arsenide*, $AsNa_3$, is prepared by heating arsenic with excess of sodium and removing the latter by liquid ammonia. It forms small black crystals.[4] The compound $AsNa_3,NH_3$, which forms brick-red crystals, is also known.[5]

Sodium Arsenates.—These salts closely resemble the corresponding phosphates, with which they are isomorphous. The normal arsenate, $Na_3AsO_4,12H_2O$, is soluble to the extent of 26·7 parts in 100 of water at 17°, and melts at 85·5°; $Na_2HAsO_4,12H_2O$, is efflorescent, crystallises from solutions below 8°, melts at 28°, and has a solubility of 56 parts in 100 of water at 14°. A second, well-defined hydrate, $Na_2HAsO_4,7H_2O$, which crystallises from solutions at 15°–20°, is quite stable under normal conditions; the crystals begin to lose water

[1] *Zeit. anorg. Chem.*, 1900, **24**, 369. [2] *Ibid.*, 1901, **28**, 177.

[3] Fleitmann and Henneberg, *Annalen*, 1848, **65**, 307; Tanatar, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 99.

[4] Lebeau, *Compt. rend.*, 1900, **130**, 502.

[5] Hugot, *Compt. rend.*, 1898, **127**, 553.

at 30°, melt at 57°, and are completely dehydrated at 120°. The anhydrous salt is readily soluble in water, 100 parts of water dissolving 61 parts at 15°; at 180°, it is rapidly converted into the pyroarsenate, $Na_4As_2O_7$.[1] The dihydrogen arsenate, NaH_2AsO_4,H_2O, is also readily soluble. An impure arsenate of sodium is prepared on the large scale by dissolving arsenious oxide in caustic soda, and adding sodium nitrate; the solution is boiled down, and the residual mass heated in a furnace until it appears to be perfectly dry. This product is largely used in calico-printing as a substitute for cow-dung, which was formerly employed in clearing the cloth after mordanting. The mordant consists of a solution of acetate of either aluminium or iron, and the cloth, after having been printed with these mordants, is hung up and exposed to air. In this, which is termed the *ageing process*, a portion of the acetic acid evaporates, leaving basic acetates of iron and aluminium firmly attached to the fibre of the cloth. A portion of these salts is, however, mixed up with the thickening or starch which must be added to the mordant in order that the impression shall be sharp. To remove this excess of unfixed mordant, the cloth is subjected to a peculiar treatment termed the *dunging process*. For this purpose it will not answer merely to wash the cloth in pure water, because the soluble portion of the mordant is then removed from the printed pattern, but attaches itself again to the unmordanted cloth, which it is intended should remain white. Long ago it was observed by the native dyers and calico-printers in India that if cow-dung be added to the wash water the excess of mordant can be removed without any staining of the cloth occurring. The action of the cow-dung in this process has not yet been satisfactorily explained, but experience has shown that sodium arsenate solution acts in a similar way, and at the present time the old process is generally superseded by the use of what is known in the trade as "dung substitute."

Borates of Sodium.

144 *Sodium Orthoborate*, Na_3BO_3.—When boron trioxide is fused with excess of caustic soda, three molecules of water are expelled and the ortho-salt remains:[2]

$$B_2O_3 + 6NaOH = 2Na_3BO_3 + 3H_2O.$$

[1] Wulff, *Apoth. Zeit.*, 1906, **20**, 1025.

[2] Bloxam, *Journ. Chem. Soc.*, 1862, 143.

This salt is very unstable; indeed it cannot exist in solution, for when dissolved in water it is transformed into a hydrated metaborate.

Sodium Pyroborate, or Borax, $Na_2B_4O_7$.—The history of this the most important of the borates is lost in obscurity. It has already been stated under boron (Vol. I., p. 714) that in the works of the Latin Geber the word borax or baurach occurs, but whether or not this indicated the substance which we now call by that name is a mere matter of speculation. Even up to the end of the seventeenth century nothing certain was known either as to the source or the composition of borax, which was used as a flux, and which was early brought into European markets by the Venetians. It was not until 1747 that an exact knowledge of its composition was arrived at, when Baron pointed out that borax consists of a compound of boric acid (then called sedative salt) and soda.

Before the discovery of the boric acid lagoons (Vol. I., p. 724) the boric acid of commerce was obtained from Asiatic tincal, which is a crude decahydrate of borax, $Na_2B_4O_7,10H_2O$, and occurs native in Tibet. Since then tincal has been found in immense deposits in North America, these being generally the bottoms of lakes which have dried up more or less completely, and large quantities are now put on the market from this source, the crude product simply requiring recrystallisation.

A large proportion of the borax used in Europe is still made from Tuscan boric acid, which is fused with half its weight of soda-ash in a reverberatory furnace, the product being lixiviated with hot water, and the borax allowed to crystallise. In France the two substances are boiled together and the product allowed to crystallise. A further source of borax is the mineral *boronatrocalcite*, $Na_2B_4O_7,2CaB_4O_7,18H_2O$, termed in commerce borate of lime or "tiza," and found in the nitrate beds of South America, and in the massive condition in Nevada; the mineral is finely divided and fused with the requisite proportion of soda-ash and sodium bicarbonate, the product being lixiviated and recrystallised.

Anhydrous Borax or Borax Glass is best obtained on the small scale by fusing 124 parts of crystallised boric acid with 53 parts of dry sodium carbonate. A transparent glass is thus obtained having a specific gravity of 2·367, which becomes opaque on exposure to air from absorption of water.

Fused borax glass dissolves many metallic oxides, which

impart their peculiar colours to the glass, and it is therefore largely used in blowpipe analysis. The constitution of this glass appears to be very complex.[1] It is readily soluble in water, but insoluble in alcohol.

Borax forms two important hydrates. *Octahedral Borax*, $Na_2B_4O_7,5H_2O$, is deposited when a supersaturated borax solution, prepared by dissolving three parts of the decahydrate (common borax) in four parts of warm water, is allowed to evaporate spontaneously in a warm place. Another plan is to dissolve borax in boiling water until the specific gravity of the solution rises to 1·246, and then allow the solution to cool. The crystallisation of octahedral borax begins when the temperature reaches 79°, and continues until it sinks to 35·5°, after which common borax is deposited. The crystals are hard, transparent, regular octahedra, having a specific gravity of 1·815.

Common, or prismatic Borax, $Na_2B_4O_7,10H_2O$.—Anhydrous borax when exposed to moist air absorbs ten molecules of water and forms this salt. The decahydrate is deposited from solutions at all temperatures below 35·5° in the form of large transparent monoclinic prisms, which have a specific gravity of 1·71. When gently heated in the air the crystals swell up, losing their water and forming a spongy mass called *borax usta*, or burnt borax.

In contact with a saturated solution the decahydrate is stable up to 35·5°,[2] and above this temperature is converted into the pentahydrate. 100 parts of water dissolve:[3]

At	5°	10°	30°	45°	50°	55°	60°	70°
$Na_2B_4O_7$	1·3	1·6	3·9	8·1	10·5	14·2	20	24·4

80°	90°	100°
31·4	40·8	52·3

The aqueous solution has an alkaline reaction[4]; hence borax is often used for purposes which require a weak alkali.

The impurities usually found in commercial borax are sodium carbonate, traces of the sulphates and chlorides of the alkali

[1] Burgess and Holt, *Proc. Roy. Soc.*, 1904, **74**, 285.

[2] van't Hoff and Blasdale, *Sitzungsber. K. Akad. Wiss. Berlin*, 1905, 1086.

[3] Horn and van Wagener, *Amer. Chem. J.*, 1903, **30**, 344; compare Poggiale, *Ann. Chim. Phys.*, 1843 (3), **8**, 467.

[4] Shelton, *Proc. Chem. Soc.*, 1902, 169; Grünhut, *Zeit. physikal Chem.*, 1904, **48**, 569; Lundberg, *Zeit. physikal. Chem.*, 1909, **69**, 442.

metals, and salts of magnesium and calcium. Sometimes it is adulterated with alum and common salt. Pure borax gives no effervescence with acids, and dissolves in two parts of hot water. The solution is not rendered turbid on addition of alkali, and does not give a precipitate either with barium chloride or silver nitrate.

Borax is largely used for a number of purposes, for glazing both earthenware, and fabrics such as linen, as an antiseptic, and also in preparing clean surfaces of metals previous to soldering.

Sodium Metaborate, $NaBO_2,4H_2O$.—This salt is formed when borax is fused with the requisite quantity of sodium carbonate. It crystallises from water in monoclinic crystals having the above composition. A pentaborate, $Na_2B_{10}O_{16},10H_2O$, has also been described.[1]

Sodium Perborate, $Na_2B_4O_8,10H_2O$.[2]—When an intimate mixture of one molecular proportion of sodium peroxide and four molecular proportions of boric acid is added gradually to cold water a clear solution is first obtained from which a perborate of the above composition crystallises out; it cannot be recrystallised from water without decomposition. On the addition of a quantity of hydrochloric acid equivalent to one half of the sodium in this perborate to its aqueous solution a perborate, $NaBO_3,4H_2O$, separates in the form of white crystals which are quite stable at ordinary temperatures. This salt is less soluble than the former. Its aqueous solution has an alkaline reaction and contains hydrogen peroxide; it begins to decompose slowly above 40° and evolves oxygen rapidly at 100°. By neutralising the solution with acids fairly concentrated solutions of hydrogen peroxide can be obtained. This compound appears to be a true per-salt as it does not contain hydrogen peroxide of crystallisation.[3]

Sodium perborate is used in laundry work and for hygienic purposes.

Sodium and Carbon.

145 *Sodium Carbide*, Na_2C_2.—When acetylene is passed over melted sodium at a temperature below 190°,[4] and when liquid

[1] Atterberg, *Zeit. anorg. Chem.*, 1906, **48**, 367; Dukelski, *Zeit. anorg. Chem.*, 1906, **50**, 38.

[2] Jaubert, *Compt. rend.*, 1904, **139**, 796; *Rev. gen. Chim. pure appl.*, 1905, (vii.), **8**, 163; Bosshard and Zwicky, *Zeit. angew. Chem.*, 1912, **25**, 938.

[3] Bosshard and Zwicky, *Zeit. angew. Chem.*, 1912, **25**, 993.

[4] Matignon, *Compt. rend.*, 1897, **124**, 775.

acetylene is treated with sodium at the ordinary temperature,[1] a white solid known as *monosodacetylene*, C_2HNa or C_2H_2,C_2Na_2, is formed. This substance is produced also by mixing liquid acetylene with a solution of sodium in liquid ammonia and crystallises in microscopic, rhombohedral lamellæ. When this compound is heated, or treated with iodine in presence of benzene, the carbide, Na_2C_2, is left as a white solid, which is also formed when acetylene is passed over sodium above 210°.

This substance has the sp. gr. 1·575 at 15°, is insoluble in all solvents, and when strongly heated in a vacuum, dissociates into its elements. It undergoes chemical change with great readiness and violence, free carbon being as a rule liberated. When gently heated in dry air or oxygen, it burns, forming sodium carbonate, and it is readily attacked by the halogen elements and by phosphorus. When it is carefully brought into water, acetylene is liberated and caustic soda produced. In hydrogen chloride it burns spontaneously, forming sodium chloride, hydrogen, and carbon.[2]

Sodium Carbonate, Na_2CO_3, commonly known as carbonate of soda or soda-ash, is prepared on an enormous scale, being one of the chief products of the alkali manufacture which is described in detail below (p. 280). The anhydrous salt is a white, opaque, porous mass or a white powder, which has a specific gravity of 2·5, melts at 852° without decomposition in absence of moisture, and possesses an alkaline taste and reaction, but less strongly marked than those of potassium carbonate. When the anhydrous salt is brought in contact with water, heat is evolved and an alkaline solution is formed. This alkalinity, as already explained (p. 102), is due to a partial hydrolysis of the salt into caustic soda and sodium bicarbonate, and it is found that a normal solution of the carbonate slowly loses carbon dioxide when it is boiled in a current of hydrogen.[3]

Owing to the existence of several different hydrates, the solubility of sodium carbonate shows an anomalous behaviour with rise of temperature, analogous to that of sodium sulphate (p. 113). The limits of stability of these hydrates in contact with a saturated solution are probably the following: $10H_2O$ from $-2·1°$ to 31·8°; $7H_2O$ from 31·8° to 35·1°; $1H_2O$ from

[1] Moissan, *Compt. rend.*, 1898, **126**, 302; **127**, 911.

[2] Matignon, *Compt. rend.*, 1897, **125**, 1033.

[3] Küster and Grüters, *Ber.*, 1903, **36**, 748. See also McCoy, *Amer. Chem. J.*, 1903, **29**, 437.

35·1° to 104·7°, the boiling point of the saturated solution.[1] One hundred parts of water dissolve :

At	0°	10°	20°	30°	31·8°	35·1°	40°	50°	70°	104·7°
Na_2CO_3	7·1	12·6	21·4	40·9	46	51	49·7	47·5	45·8	45·1.

The *decahydrate* is obtained when a hot, fairly concentrated solution is allowed to cool, and forms large, transparent monoclinic crystals, which are known commercially as *soda-crystals* or *washing soda*, and are manufactured on the large scale. They readily effloresce on exposure to the air, yielding the monohydrate as a white powder, which is also formed by heating the decahydrate to 35·1°, at which temperature it melts and loses nine molecules of water. The *monohydrate* crystallises in rectangular, rhombic plates, and is prepared commercially and sold under the name of *crystal carbonate*. Both of these hydrates occur native, the former as *natron* and the latter as *thermonatrite*, in the soda lakes of Egypt[2] and Hungary, and also at Vesuvius and Etna, and in various parts of Asia, Africa, and America.

Of the remaining hydrates the *heptahydrate*, $Na_2CO_3,7H_2O$, is the most important, and is obtained by allowing a warm saturated solution to cool in absence of air; it appears to be dimorphous, crystallising both in rhombohedra and rectangular rhombic plates.

Commercial anhydrous sodium carbonate prepared by the Leblanc process always contains sodium chloride and sulphate, as well as caustic soda and other impurities. That prepared by the ammonia soda process contains as a rule only sodium chloride as impurity. Soda crystals are usually much purer, and may be obtained perfectly free from impurity by repeated crystallisation.

Sodium Hydrogen Carbonate, $NaHCO_3$.—This salt, commonly known as bicarbonate of soda, is likewise prepared on the large scale. It occurs in commerce in the form of a white, crystalline powder, or in crystalline crusts which consist of monoclinic tablets. It possesses a faint alkaline taste, and dissolves less readily in water than the normal salt. A solution of the

[1] Ketner, *Zeit. physikal. Chem.*, 1902, **39**, 645; Epple, *Diss. Heidelberg*, 1899, p. 26, quoted in *Physikalisch-Chemische Tabellen*, Landolt-Börnstein, p. 555 (Berlin, Springer, 1905); Wells and McAdams, *J. Amer. Chem. Soc.*, 1907, **29**, 721; Jones, *Journ. Chem. Soc.*, 1909, **95**, 1672; Cumming, *ibid.*, 1910, **97**, 593.

[2] *Jahrb. Min.*, 1900, i., 236.

bicarbonate is neutral to phenolphthaleïn, but alkaline to methyl orange. One hundred parts of water dissolve :[1]

At	0°	10°	20°	30°	40°	50°	60°
$NaHCO_3$	6·90	8·15	9·60	11·10	12·70	14·45	16·40.

A solution of the bicarbonate gives off carbon dioxide on boiling, forming first the carbonate (trona) $Na_2CO_3,NaHCO_3,2H_2O$;[2] this carbonate is formed also when carbon dioxide is passed into a boiling solution of the normal carbonate and when solutions of the latter are exposed to the air for some time. The solid salt decomposes on gentle ignition into carbon dioxide, water, and the normal salt:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Commercial bicarbonate of soda almost always contains some normal carbonate, and this may be removed by washing with small quantities of water ; but, on drying, the residual salt is found again to contain some normal carbonate. A better method is to moisten the washed salt with alcohol, and then to dry it between folds of filter paper without application of heat. Even then it undergoes partial decomposition, and contains about one per cent. of the normal carbonate. In order to detect the presence of the latter salt in the bicarbonate a solution of mercuric chloride in two parts of water is added to a solution of the bicarbonate in fifteen parts of water, when a white cloudiness, which gradually becomes brown after several minutes, is produced in presence of the normal salt; this test, however, is only of an approximate character, as the presence of the normal carbonate can be proved with certainty only by a quantitative examination.

Trona, or Urao, is a carbonate of soda occurring native in Hungary, Egypt, British East Africa, Fezzan and Lake Chad in Africa, India, and America. It is a compound of the normal with the bicarbonate, and has the formula $Na_2CO_3,NaHCO_3,2H_2O$.[3] This is the substance to which the ancients gave the name *nitrum.* It occurs in small monoclinic crystals, and it can be prepared artificially as described above.

[1] Dibbits, *J. pr. Chem.*, 1874 (2), **10**, 439.

[2] Soury, *Compt. rend.*, 1908, **147**, 1296 ; Habermann and Kurtenacker, *Zeit. anorg. Chem.*, 1909, **63**, 65.

[3] Compare Lunge, *Sulphuric Acid and Alkali*, Vol. II., pp. 52 and 55, 3rd edition, 1909. Also "Egyptian Soda" Survey Department Paper No. 22, *Nature*, 1913, **90**, 527.

Sodium Percarbonate has already been described[1] (Vol. I., p. 825).

Sodium Cyanide, NaCN.—This salt is obtained by neutralising hydrocyanic acid with soda, and by heating sodium ferrocyanide either alone or with metallic sodium (see also potassium cyanide):

$$Na_4Fe(CN)_6 = 4NaCN + FeC_2 + N_2$$
$$Na_4Fe(CN)_6 + 2Na = 6NaCN + Fe.$$

When obtained by passing hydrocyanic acid into alcoholic soda it is a white, crystalline powder, which smells of hydrocyanic acid, and dissolves readily in water.

It is now manufactured on the large scale by Castner's method,[2] which consists in passing ammonia over metallic sodium heated in an iron retort to 300–400°, yielding sodamide according to the equation:

$$2Na + 2NH_3 = 2NaNH_2 + H_2.$$

This is then brought into contact with charcoal previously heated to dull redness, and thus coverted into sodium cyanamide and hydrogen:

$$2NaNH_2 + C = CN.NNa_2 + 2H_2.$$

At a higher temperature, in presence of the excess of charcoal, the cyanamide is then converted into sodium cyanide:—

$$CN.NNa_2 + C = 2NaCN.$$

The product is almost pure.

Calcium cyanamide ("Nitrolim") also is used for the preparation of sodium cyanide (Vol. I., p. 853).

Sodium cyanide, like the potassium salt, is now very largely employed for the extraction of metallic gold.

Silicates of Sodium.

146 Silica acts on sodium carbonate at high temperatures with evolution of carbon dioxide and formation of silicates, different silicates being obtained according to the time of heating, the temperature, and the relative proportions of the

[1] Compare also:—Tanatar, *Ber.*, 1910, **43**, 127, 2149; Riesenfeld, *ibid.*, 1910, **43**, 566, 2594; 1911, **44**, 3589, 3595; Wolffenstein, *ibid.*, 1910, **43**, 639.

[2] Patent No. 21732 (1894).

two substances taken. Unlike potassium, however, sodium is capable of forming an *orthosilicate*, Na_4SiO_4, whilst the silicate richest in potassium is $K_8Si_3O_{10}$. If silica and sodium carbonate be fused together in equal molecular proportions, *sodium metasilicate*, Na_2SiO_3, is formed, and of this compound a number of definite crystalline hydrates have been obtained, crystallising with from 1 to 9 molecules of H_2O. The solution of this substance in water is strongly alkaline, and probably contains half the sodium as caustic soda, together with the silicate $Na_2Si_2O_5$.[1]

Soluble Soda Glass, which was discovered by Fuchs in 1818, is obtained by heating together 180 parts of white sand, 100 of calcined soda-ash, and 3 of charcoal in a reverberatory furnace, and also by dissolving powdered flint in hot aqueous caustic soda under pressure. Like the corresponding potash glass it consists of a mixture of several silicates, the melting point being higher the greater the proportion of silica present. Prepared by the first method, soluble soda glass forms a transparent glassy mass, sometimes colourless, but generally of a yellow, brown, or green colour, which when powdered, readily dissolves in boiling water, forming a thick viscid liquid. When concentrated ammonia is added to the solution, a silicate having approximately the composition $Na_2Si_4O_9$ separates out,[2] and a hydrate of this silicate, containing $12H_2O$, is formed when precipitated silica is dissolved in boiling caustic soda and the filtrate evaporated down.[3]

Silicate of soda is employed in fixing fresco colours by the process of stereochromy. It is employed also as a cement in the manufacture of artificial stone. This is made by mixing the solution with sand and lime; it is likewise used as a cement for joining the broken surfaces of porcelain, stone, &c. Another purpose for which soluble glass is employed is as an addition to cheap soap. The so-called silicated soap, the preparation of which was patented early in the last century and which was subsequently largely made by William Gossage, who also took out a patent for its manufacture, is now prepared in large quantities by adding a solution of this compound to the soap whilst settling.

[1] Kohlrausch, *Zeit. physikal. Chem.*, 1893, **12**, 773; Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 295; Mylius and Groschuff, *Ber.*, 1906, **39**, 116.

[2] Heintz, *Jahresb.*, 1871, 276.

[3] Walker, *Quart. Journ. of Science*, 1866, **3**, 371.

Sodium Silicofluoride, Na_2SiF_6, is prepared in a similar way to the potassium compound, and is very similar to this latter salt; 100 parts of water dissolve at 17·5°, 0·652 part of the salt, and at 101°, 2·459 parts (Stolba).

Detection and Estimation of Sodium.

147 The presence of a sodium compound can be readily detected by the production of the yellow tint which it imparts to the non-luminous gas-flame. This reaction was first observed by Melville in 1752, and was made use of by Marggraf in 1759 to distinguish the base contained in common salt from that peculiar to the vegetable alkali, which imparted a violet tint to the flame.

The spectrum of the yellow sodium flame consists of two bright yellow lines coincident with the two dark solar lines known as Fraunhofer's D-lines. These lines have wave-lengths of 5896 and 5890 A.U. and lie so close together that in an ordinary one-prism spectroscope they appear as one line.

The flame reaction of sodium is the most delicate known among spectrum reactions, as has already been mentioned (p. 158).

The absorption spectrum of sodium vapour has been mapped by Roscoe and Schuster.[1] A series of bands in the blue makes its appearance at a low temperature, and as this is raised bands in the red and yellow stretching as far as the D-lines come out. When the vapour of sodium is examined in a red-hot iron tube the colour of the limelight as seen through it is a dark blue.

In the processes of quantitative analysis sodium generally occurs together with potassium. The process for the separation of these two metals is described under that metal, as well as the indirect methods by which the quantity of each of the two metals can be ascertained. If it is desired to determine the sodium directly, the best process is the following one suggested by Bunsen. The alcoholic solution of the soluble double chloride of sodium and platinum is evaporated in a flask which is filled with hydrogen gas, and reduced by exposure to light, or by addition of a reducing agent such as aldehyde. Sodium chloride, hydrochloric acid, and metallic platinum are then formed: the solution of common

[1] *Proc. Roy. Soc.*, 1874, **22**, 362.

salt is filtered from the platinum, evaporated to dryness, and the weight of the salt ascertained after gentle ignition. As sodium chloride is volatile at a red heat, it is advisable to transform the salt into sulphate before ignition.

Sodium, moreover, forms sparingly soluble salts of antimonic acid and of dihydroxytartaric acid,[1] and can be estimated in presence of potassium by precipitation with the potassium salt of either of these acids.[2]

The atomic weight of sodium was determined by Stas. He found as the result of ten experiments that 100 parts by weight of pure silver required from 54·206 to 54·2093 parts of sodium chloride for complete precipitation. This gives a mean of 54·208, and the atomic weight of sodium as 23·05.

This ratio has been redetermined by Richards and Wells,[3] who employed more perfectly purified silver, and estimated the end point of the reaction between silver nitrate and sodium chloride by means of a specially devised instrument, the nephelometer.[4] The ratio obtained was Ag : NaCl = 100 : 54·185, whilst that of AgCl : NaCl was 100 : 40·780. Hence, taking the accepted values for silver (Ag = 107·88) and for chlorine (Cl = 35·46), these results give 22·99. The value now adopted is 23·00.

THE ALKALI MANUFACTURE.

148 The history of the manufacture of the alkali, soda, is one of great and peculiar interest. The following is a description (1) of the oldest known sources and processes, (2) of the Leblanc process, (3) of the cryolite process, (4) of the ammonia process, and (5) of the electrolytic processes, followed by a description of the several forms in which the alkali now appears in commerce. A great number of other proposals for the manufacture of soda have been made, for details of which reference may be made to Lunge, "Sulphuric Acid and Alkali Manufacture" (3 vols. London, Gurney and Jackson). The manufacture of bleaching powder is described separately under calcium.

[1] Fenton, *Journ. Chem. Soc.*, 1898, **73**, 167.
[2] Bulstern and Blaise, *Zeit. anal. Chem.*, 1897, **36**, 513.
[3] *J. Amer. Chem. Soc.*, 1905, **27**, 459.
[4] *Amer. Chem. J.*, 1904, **31**, 235.

The Oldest Known Sources and Processes.

149 *Natural Soda.*—From time immemorial an alkali has been obtained as a saline efflorescence from the ground in parts of Egypt, and from certain alkali lakes in that country; the substance is known as trona or latroni, and it contains about 20 per cent. of "sodium sesquicarbonate" $Na_2CO_3,NaHCO_3,2H_2O$ (see pp. 276 and 317); it is still exported from Alexandria at the rate of about 2,500 tons per annum. Nearly every district of India produces alkaline earth, known as dhobies earth, containing from 11–36 per cent. of the double carbonate, which has been used for ages for washing, dyeing, and in the manufacture of soap and glass bangles. Very many districts are so impregnated with alkali that they form wastes or alkali deserts, as in Tibet and Utah. At Owens Lake in California the water is so nearly saturated with alkali that shallow receptacles are filled with it and then allowed to evaporate spontaneously, after which the crystals receive a slight wash to purify them; it is computed that this lake contains 50,000,000 tons of soda; and that the annual increase is 200,000 tons; and it is expected that the American market may in time be supplied from this source. In 1910 a great deposit of soda was found and explored in Lake Magadi, East African Proctorate. The lake covers an area of 30 square miles; the reddish water is only a few inches deep, and under this is a deep layer of natural soda in large, radiating crystals looking like pink marble, which is estimated to weigh 200,000,000 tons, and which might supply the world for 100 years. This is being developed by the Magadi Soda Company, who are building 100 miles of railway to connect with the Uganda Railway, while the Government are preparing to deal with the transport on the Uganda Railway and to give loading facilities for ocean shipping at Kilindini.

Soda from Plant Ashes.—From very old times it has been known that the ashes of plants contained alkali, and they were used for cleansing, and for making soap and glass. Whereas almost all land plants yield an alkali that is mostly potash, certain land plants growing near the sea shores yield an alkali that is mostly, but not entirely, soda; such plants are grown on the Spanish coasts, and they have been cut and burned for centuries to prepare the ash barilla, which never contains more than 30 per cent. sodium carbonate and often only 3 per cent.; in

1834 even the import of this Spanish soda into this country was 12,000 tons, and it realised £11 to £45 per ton. Sea plants yield an ash that is still poorer in potash and richer in soda, and these were cut or collected on the North-west coasts of France, Ireland, and Scotland, and burned to prepare an ash containing only 2½ to 5 per cent. soda, known as "kelp." In the Orkney Islands a large number of persons used to be engaged in this work. Kelp is now used as a source of potassium chloride and of iodine. Land plants contain portions of soda which are not inconsiderable, and in the manufacture of beet-root sugar the residual molasses finally yield a charcoal from which soda is extracted in France, Germany, Austria and Belgium, to the extent of 2,500 tons per year.

Oldest known chemical processes of preparing soda.—In 1768 Hagen described the double decomposition between sodium sulphate and potassium carbonate; the less soluble potassium sulphate crystallises first from the solution, and soda crystals were then obtained from the mother liquor. This process was also described by Accum as being carried out in a soda works in London prior to 1808. A similar double decomposition due to Bergmann was carried out with sodium chloride and potassium carbonate; and some years later, in 1795, Lord Dundonald obtained a patent connected with the process, and from 1802–1815 at Walker-on-Tyne Losh made soda called "British Ash" which sold for £16 to £20 per ton.

Other processes for the manufacture of soda independently of potashes, but in which organic materials were used, have been suggested; thus in 1778 Crell precipitated calcium acetate with sodium sulphate to obtain a solution of sodium acetate, which on evaporation and ignition left sodium carbonate, and in 1789 Kirwan precipitated lead acetate solution in the same way and for the same purpose. Strictly inorganic processes were also employed. In 1773 Scheele reacted on sodium chloride solution with oxide of lead, obtaining an insoluble oxychloride of lead and a solution of caustic soda; in 1782 soda was being made in England by this process, and in 1787 Turner patented a yellow lead oxychloride, a pigment known as Turner's yellow.

But the most important of these inorganic processes for subsequent developments was that of Malherbe in 1778. He heated sodium sulphate with carbon, obtaining sodium sulphide, and to the molten mass added iron scrap to combine with the sulphur. After due manipulation in the furnace the

melt was withdrawn and the blocks allowed to stand in the air until they fell to powder, which, when lixiviated, gave a solution from which soda crystals were at once obtained. The similarity of this process to that next described, in all particulars except the use of iron, may be noted.

The Leblanc Process.

150 One of the effects of the French revolutionary wars was the stoppage of the supply of potashes to France, and therefore the diminution of the important manufactures dependent upon its use. Under these circumstances the French Government issued an appeal to chemists urging the importance of utilising all the materials natural to their own country, "so as to render vain the efforts and hatred of despots," and commanded all citizens who "have commenced establishments or who have obtained patents for the manufacture of soda from common salt, to make known to the Convention the locality of these establishments, the quantity of soda supplied by them, and the quantity they can hereafter supply." A Commission was appointed to investigate this subject, and in 1794 it reported on thirteen different processes, the particulars of which had been submitted. The preference was given to the operations devised by an apothecary of the name of Leblanc, who had erected a soda manufactory at Franciade, near Paris; this had been at work for about three years. The process which constituted Leblanc's invention consisted of the conversion of common salt by vitriol into Glauber's salt, whilst the evolved hydrochloric acid was converted into sal-ammoniac. The sulphate of soda was mixed, according to Leblanc's first description in 1790, with half its weight of chalk and a quarter of its weight of charcoal, but, according to his Patent of 1791, with an equal weight of chalk and half its weight of charcoal, which proportions had yielded the best results; from the surface of the fluxing mass a large number of flames broke forth similar to the flame of a candle. As soon as this phenomenon ceased the operation was finished. The batch was drawn out of the furnace with iron rakes, and collected in any kind of moulds to give it the shape of the commercial blocks of soda of that time. The fluxed mass was purified by powdering and boiling with water, or else it was allowed to fall to powder in the air and then washed. The calcareous substance

and unburnt charcoal were removed by settling and filtering. From the solution the soda was separated on boiling down, and dried in a warm place.

Why Leblanc should have reacted with calcium carbonate on his fused sodium sulphide is not clear, because the first explanation of Leblanc's process was given in 1830 by Dumas, who, believing that calcium sulphide was soluble in water, supposed the existence of insoluble oxysulphide, 2CaS,CaO. The existence of this hypothetical compound was first doubted in 1858 by Kynaston, and disproved by Scheurer-Kestner in 1862; and in 1861 Gossage proved that calcium sulphide was insoluble in water. The Commissioners of 1794 say in their report:— "Citizens Leblanc, Dizé, and Shée were the first who submitted to us particulars of their process, and this was done with a noble devotion to the public good." The consequences of the French Revolution and subsequent war deprived Leblanc of funds, owing to which the works were suspended from 1794 to 1801, and he was unable to work his process. It is sad to have to relate that the man who thus originated a world-wide industry, and to whom we owe cheap soap and cheap glass, did not benefit from his discoveries, and, not receiving the reward promised by his Government, died in 1806 by his own hand in poverty and despair.[1]

Other alkali works in France were more successful than Leblanc's original manufactory. Several of these were situated at Marseilles, the seat of the French soap trade, and conveniently placed for obtaining three of the necessary raw materials; (1) sulphur, imported from Sicily; (2) salt, obtained by the evaporation of salt-water by the sun's heat; (3) limestone. They were, however, at a disadvantage in being at a distance from coal.

Although the process for making alkali was published in the *Annales de Chimie* for the year 1797, it is remarkable that not till 1814 was this process taken up in England by Losh, on the Tyne, on an exceedingly small scale. In 1823 the salt duty of £30 per ton was abolished, and the way being thus opened for the use of salt as a raw material for the production of an artificial soda, which could compete with the natural sodas and the various soda ashes from plants, the same year saw the erection of an alkali works in Liverpool by James Muspratt. To prove the superiority of his product to the

[1] "Nicolas Leblanc: sa vie et ses travaux," by Aug. Anastasi, Paris, 1884.

natural sodas and plant soda ashes Muspratt had at first to give his product away, but he soon established a growing industry.

It must not be supposed, however, that Leblanc's process was complete in all its details, or was suited without alterations to English industrial requirements.

The hydrochloric acid evolved in the salt-cake process was not converted into sal-ammoniac as Leblanc had devised, but was allowed to escape into the air as a waste product, which destroyed vegetable life of all kinds for miles around, leading to complaints of nuisance and to frequent litigation. Hardly an assize passed without an action for nuisance or damage, and the present generation can scarcely form an idea of the prejudice aroused against alkali works for the first forty years of their existence. In 1836 Gossage introduced his plan of condensing hydrochloric acid, and though in the next ten years it was adopted by many works, yet many others, especially the smaller ones, continued to manufacture sulphate of soda without condensing the hydrochloric acid, and even those works which had condensers used them only in proportion as they found a sale for hydrochloric acid. The use of chlorine made from hydrochloric acid for manufacturing bleaching powder was extended from 1837 by the reduction of the excise duty on paper from 3*d.* to 1½*d.* per pound, which led to a greatly increased demand. In 1847 chlorine made from hydrochloric acid was first used on a large manufacturing scale for the preparation of potassium chlorate. In 1861 the paper duty was abolished, and with the consequent establishment of a vast number of daily and weekly newspapers and journals, and the reprinting of standard works in all parts of the kingdom, an enormously increased demand for paper materials was created. Straw, esparto grass, and wood fibres, which had hitherto been used only in very small quantities as compared with cotton and linen rags, were now used in rapidly increasing quantities, and as these require roughly three times as much bleaching powder per unit weight of raw material as do the rags, and as they produce much less weight of paper, it is evident that the demand for hydrochloric acid was vastly increased. It was computed that in 1862 one-third of all the hydrochloric acid gas produced was still allowed to escape into the air, a fraction which amounted to about 1,000 tons per week; and this nuisance was only brought to an approximate end by the passing of the

Alkali Act in 1863, which rendered compulsory the condensation of 95 per cent. of the hydrochloric acid gas produced. Thanks to the increased uses for and value of hydrochloric acid, the statutory condensation was rapidly obtained and exceeded. In 1874 another Act was passed requiring that the exit gases shall not contain more than 0·2 grain of hydrochloric acid per cubic foot of gas, and this limit is now fully observed. The means employed to condense the hydrochloric acid gas are described under the head of Hydrochloric Acid (Vol. I., p. 205). Where an acid was produced too weak to use or sell it was run away to waste, thereby often creating a fresh series of nuisances by reason of it finding its way into the drainage from the waste heaps of the lixiviation process—a liquor loaded with soluble sulphides.

The black-ash produced up to 1823 contained only 10 to 12 per cent. alkali (Na_2O), and though Leblanc had shown how to prepare from this, as his final product, a nearly pure hydrated sodium carbonate, "soda crystals," $Na_2CO_3{,}10H_2O$, yet this was not done commercially, and the black-ash was sold as such and with all its impurities to soap makers; in 1823 it realised £12 per ton. A black-ash containing 24 per cent. alkali, that is, double the previous strength, was first made by Muspratt in 1823, since when the strength has not been materially increased.

The details of the economical lixiviation of the black-ash, and the evaporation of the liquor by the waste heat from the black-ash furnaces, are due not to Leblanc but to English alkali makers, who produced in quantity not only Leblanc's "soda crystals," but also a new and much stronger alkali, namely, the white-ash or soda-ash, selling at £22 per ton in 1833. It consisted of impure anhydrous sodium carbonate, and according to its impurities and methods of preparation contained from 48 to 52 per cent. of alkali. The impurity present in largest quantity in the alkaline liquor was sodium hydrate, and this was carbonated either by adding a considerable quantity of sawdust, or by leading in waste furnace gases, or carbonic acid gas.

To the English alkali makers also is due a further development in the making of strong alkali, which was entirely new. The first step was the introduction of "caustic ash" a mixture of anhydrous sodium carbonate and sodium hydrate, obtained by using a larger proportion of lime than previously in the black-ash mixing, and by not adding sawdust or carbonic acid

gases when evaporating the alkaline liquor to dryness. About 1850 this was followed by methods of separating the bulk of the sodium carbonate as the monohydrate, Na_2CO_3,H_2O, from the liquor, and evaporating the mother-liquor, now containing essentially sodium hydrate, until it contained 60 per cent. of alkali and on cooling solidified into a crystalline mass known as "cream caustic." About 1857 the methods of removing the various impurities were improved, and the caustic liquor was evaporated at much higher final temperatures, so that anhydrous white caustic soda containing 70 per cent. alkali was obtained. In 1861 Lancashire furnished 4,680 tons of caustic soda, but in 1862 methods had been found at St. Helen's of so altering the charge in the black-ash furnace, and so working the liquor as to obtain stronger and whiter caustic soda, which at once found extended use in soap and paper manufactories. From 1873 the developments were stimulated by the success of Solvay's Ammonia Soda Process in making soda ash of excellent quality and in a very economical manner; but he could not make caustic soda except by an additional operation. By 1878 the output of caustic soda by the modified Leblanc process reached 94,000 tons a year. In 1888 the methods of separating the impurities from the raw caustic soda solutions had been so improved by the Greenbank Alkali Company that the finished caustic soda contained 77 per cent. alkali, a figure which is even now only slightly exceeded.

Lastly, the process of Leblanc left the insoluble portion of the black-ash as great mounds of waste creating a general nuisance that led the manufacturers into great trouble for many years. The waste underwent oxidation, and rain and drainage waters dissolved from it soluble sulphides, polysulphides, and thiosulphates, which found their way into the drains and streams of the district, whither also was discharged the waste weak hydrochloric acid made in the early years of the process; and the resultant sulphuretted hydrogen was sufficient to be a nuisance to the inhabitants of districts lying even several miles away from the waste. With improvements in the construction of the salt-cake furnaces, and also in the condensing towers for the hydrochloric acid, the production of waste weak acid was stopped and with it the production of sulphuretted hydrogen. But the drainage of the sulphide liquors from the heaps continues to kill all life in the water courses. Many processes have been tried to turn the waste calcium sulphide to useful account, as by

Gossage in 1837, at Stoke Works, near Bromsgrove, followed by Schaffner in Germany, and Mond in England. The latter tried to carry on intentionally the above described unintentional operations, except that the atmospheric oxidation was to be carried on so far that there should be sufficient thiosulphate present to destroy all the sulphuretted hydrogen, when the waste weak acid was added, and consequently the combined sulphur in both sulphurous acid and sulphuretted hydrogen was precipitated in a pure and useful form. When waste weak acid was no longer available this process was abandoned, and it was not till 1888 that in the Chance-Claus process a

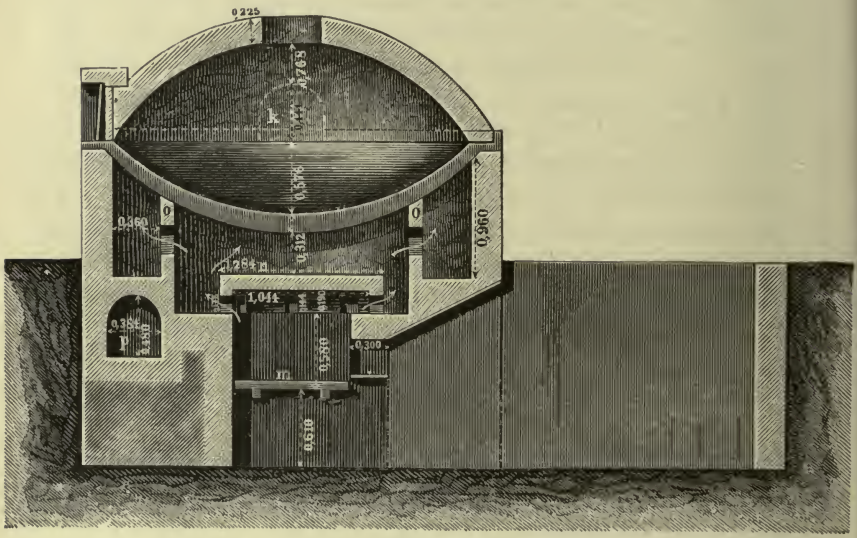


Fig. 84.

satisfactory method was discovered of ending the nuisance and recovering the contained sulphur in a form of much greater value than that in which it was introduced; the process is described later (pp. 301–303).

151 (1) *The Salt-cake Process.*—This process is usually commenced in large cast-iron pans nine feet in diameter but scarcely two feet deep. Through the doorway shown in the upper left hand corner of Fig. 84 is introduced the charge of 16 cwt. of common salt, and on to this is run the quantity of sulphuric acid necessary to decompose it completely. This amounts to 123·5 gallons, or 1,800 lbs. of chamber acid having a specific gravity of 1·42. Torrents of hydrochloric acid are

given off, and the temperature of the mass rises to about 50°. All the strong hydrochloric acid gas which is thus evolved, being confined by the brick covering of the pan, the closed charging door, and the closed discharging door indicated by *k* in Fig. 84, passes through the central opening in the cover, and is sucked through a set of attached earthenware pipes into the hydrochloric acid condensing towers, described under the heading of Hydrochloric Acid (Vol. I., p. 205). When the evolution of gas begins to slow down the pan is heated, with considerable precautions to avoid local overheating. After about one hour's heating the product is essentially a mixture of sodium hydrogen sulphate and common salt,

$$2NaCl + H_2SO_4 = NaHSO_4 + NaCl + HCl,$$

which will not react further unless the temperature is raised to a

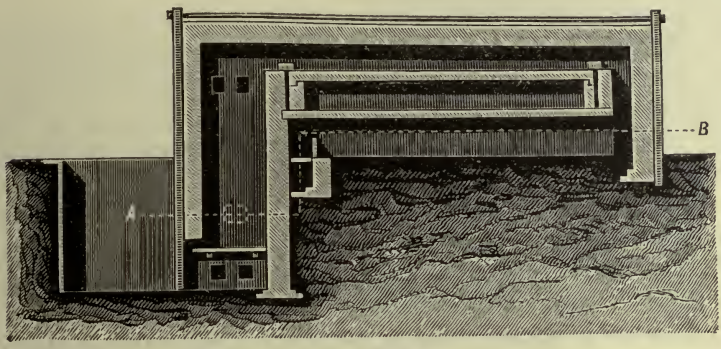


FIG. 85.

much higher degree than the cast-iron pot will stand. The mixture is therefore raked through the door indicated by *k*, Fig. 84, on to the firebrick hearth of an adjacent "roaster."

The roasters were at first simple reverberatory furnaces, which have since been modified mainly in order to obtain the strongest possible hydrochloric acid gas which is easy of condensation, but also to avoid contamination of the salt-cake with the ashes of the fuel. The older forms of roasters being no longer permitted to be erected, only the present form, due to Deacon of Widnes, is described; it is shown in Fig. 85. The fireplace is built contiguous to, but several feet below the brick chamber or muffle in which the salt-cake is roasted and the acid gas is evolved, and the exhaust flue is not above, but under the ground level.

With these modern furnaces it is comparatively easy so to

regulate the draught on the furnace and the draught on the muffle and attached condensers that the pressure in the flue round the muffle is slightly greater than that in the interior of the muffle, thus preventing the passage of the acid gas from the muffle through the unavoidable cracks into the chimney, although allowing some of the fire-gases to pass into the muffle, but in such regulated quantity that they do not interfere with the successful working of the condensation.

Many attempts have been made to carry out the manufacture of salt-cake in mechanical furnaces, among which may be mentioned those of Jones and Walsh, Cammack and Walker, and Mactear.[1] The revolving furnace of the latter has been the most successful in practice, and consists of a circular revolving bed covered by a fixed arch, between which and the bed the furnace gases pass. The salt and acid are constantly fed into a large cup in the centre of the hearth, where they mix and overflow into the outer portion of the circle, and are subjected to the action of the hot gases; by means of fixed stirrers the mass is continuously mixed and gradually worked to the circumference, over which it then falls. The action is thus a continuous one, and the amount of hydrochloric acid evolved is therefore constant, so that in spite of the fact that the acid-gas is mixed with the whole of the furnace gases, the condensation is carried out more readily and a more concentrated acid is obtained than in the ordinary process.

Another important process for making salt-cake is that of *Hargreaves*. The object of this is to dispense with the manufacture of sulphuric acid, and it depends upon the fact that, although sulphur dioxide cannot by itself decompose salt, it is able to do so in the presence of oxygen and water, if sufficient time be allowed for the reaction. In order to effect this decomposition, a series of large kilns or stoves, built of brick, is so arranged that each kiln can be put into communication with its neighbour, and each heated by a fire. Each kiln is then filled with specially prepared cakes of dried and porous salt, and the gases from the pyrites burners are led directly into these kilns arranged in series. By careful attention to temperature and to the quantity of air and steam admitted with the sulphur dioxide, it is possible to decompose the salt as perfectly as by the old process with sulphuric acid:

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

[1] *Proc.* First General Meeting, Soc. Chem. Ind., 1881, **26**.

The hydrochloric acid gas is separated from the accompanying residual nitrogen in the hydrochloric acid condensing towers.

The following is an average analysis of salt-cake :

Na_2SO_4	$NaHSO_4$	NaCl	$CaSO_4$	Fe_2O_3 and insoluble	H_2O
95·27	1·48	1·35	0·92	0·32	0·18 = 99·52.

152 (2) *The Black-ash Process.*—The theory of this process, as given by Scheurer-Kestner and Pelouze, is a simple one, so far as the chief products are concerned, but it is complicated by many secondary reactions, and by the impurities in the raw materials.

When the salt-cake is heated with slack, or powdered coal,

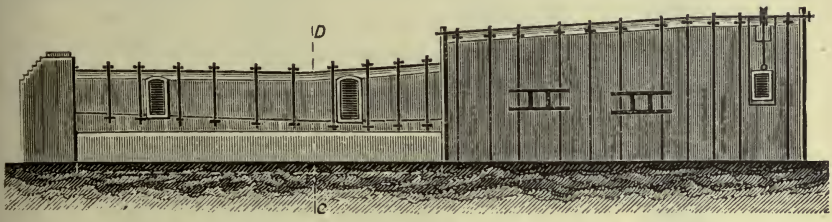


FIG. 86.

it behaves like all other fairly stable sulphates, being converted into the corresponding sulphide, thus: [1]

$$Na_2SO_4 + 2C = Na_2S + 2CO_2,$$

and the characteristic part of the Leblanc process is the heating of the sodium sulphide with chalk or limestone (calcium carbonate), whereby sodium carbonate and calcium sulphide are formed, of which the former is exceedingly soluble in water at a little under 50° C., and the latter is insoluble in water of the same temperature:

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

In practice these two reactions are made to take place simultaneously, by mixing about 10 parts by weight of salt-cake, 10 parts of limestone, and 5-7 parts of coal, and heating the same in a reverberatory furnace, termed a balling furnace. The right-hand halves of Figs. 86 and 87 show the elevation and longitudinal section of such a furnace, and Fig. 88 shows

[1] Kolb, *Ann. Chim. Phys.*, 1866 (4), **7**, 118 ; Lunge and Fischer, see Lunge, *Sulphuric Acid and Alkali*, 1909, Vol. II., Part II., p. 521.

the transverse section on the line A B looking towards the fire-place.

After exposure to the reducing flames from the furnace for two hours, with frequent stirring, the end of the operation is indicated by the appearance of yellow flames or "candles" on the surface of the melt, due to the formation of carbonic oxide

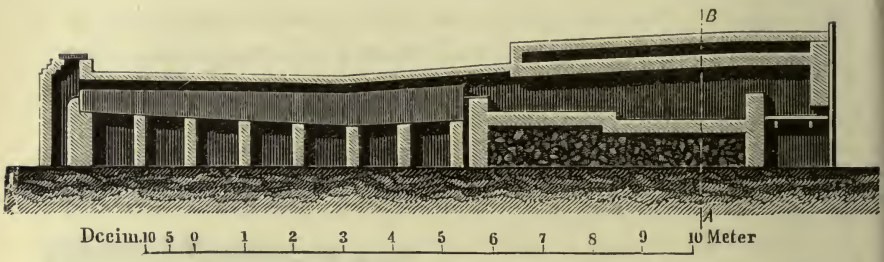


FIG. 87.—Longitudinal Section through Fig. 86.

at the elevated temperature of the furnace by the action of carbon on calcium carbonate:

$$C + CaCO_3 = 2CO + CaO;$$

this evolution of gas is also of importance for the subsequent lixiviation of the black-ash, as it renders the mass porous.

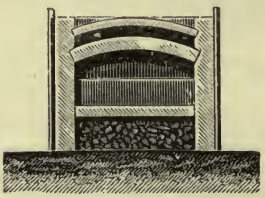


FIG. 88.
Section through A B of Fig. 87.

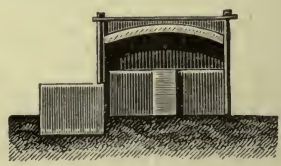


FIG. 89.
Section through C D of Fig. 86.

The liquid mass is scraped out into iron barrows or trucks and allowed to cool, and in this state is known, from the colour of the mass, as black-ash ball.

In place of the old black-ash furnace or balling-furnace, in which the mixing of the materials is effected by hand labour, a furnace termed a revolving black-ash furnace is now largely employed, the general arrangement of which is shown by the left-hand side of Fig. 90 and in Fig. 91 and also in Figs. 93, and 94. In this the mixing of the materials is effected mechanically. The charge of about 4 tons is introduced by

means of a hopper into a large horizontal cylinder (B), through which flames from a furnace (A) are allowed to pass; this

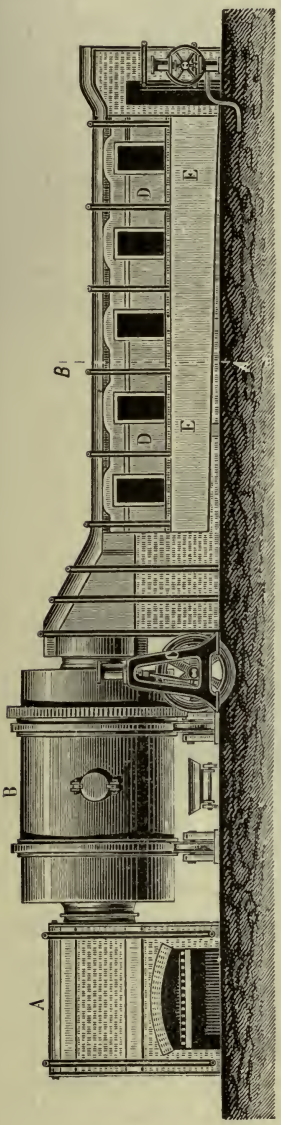


Fig. 90.

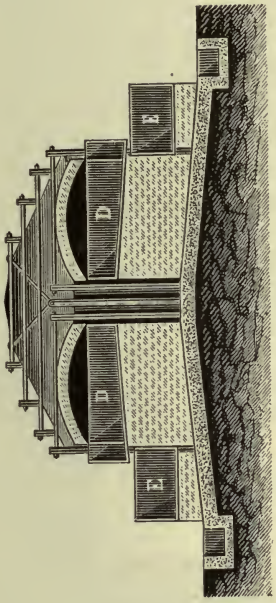


Fig. 92.
Cross Section at A B in Fig. 90.

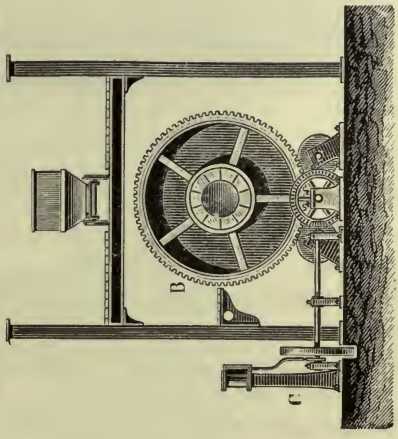


Fig. 91.

cylinder, worked by an engine (C), revolves first at a slow rate, afterwards increasing to a maximum velocity of five or six revolutions per minute. The cylinder is from 10 to 12 feet in

diameter and generally from 15 to 18 feet long, but they have also been made up to 30 feet long.[1] Each charge takes about two hours, and when completed the charging hole in the side of the cylinder is opened, and by slowly moving the cylinder to bring the hole lower and lower, the fused mass is forced to flow into a series of iron trucks placed beneath it. Another method of heating the black-ash revolver is shown in Fig. 93 and in the left-hand side of Fig. 94. In this arrangement the revolver (F) is fed with gas from a Siemens gas-furnace, and the regenerators (NN) for the recovery of the waste heat are placed below the revolver.

The advantages of the revolving black-ash furnace over the hand-worked ones consist chiefly in the saving of labour

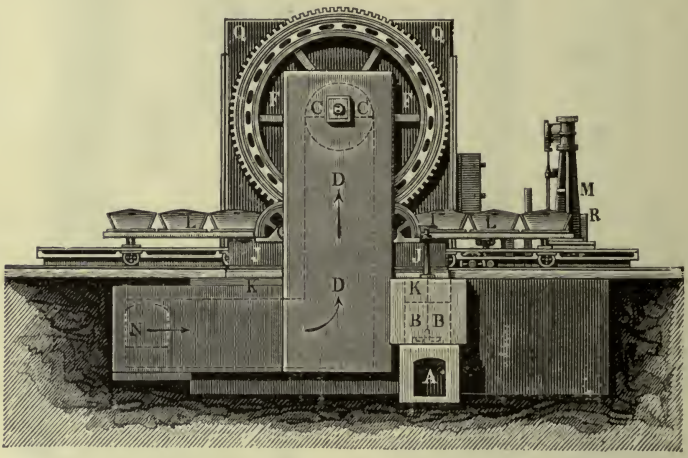


FIG. 93.

and the production of a material which possesses a more constant composition. The best results are obtained by adding for a given quantity of salt-cake a considerable excess of coal, as this burns away prematurely, but only the theoretical amount of limestone; when the reaction is complete, there is added to each 100 parts of salt-cake originally taken a further quantity of 7 parts of salt-cake and 7 parts of limestone. The addition of the salt-cake destroys the cyanides formed from the nitrogen of the coal by utilising their powerful reducing action:

$$2NaCN + Na_2SO_4 = Na_2CO_3 + Na_2S + CO + N_2,$$

[1] Smith, *Journ. Soc. Chem. Ind.*, 1887, **6**, 416.

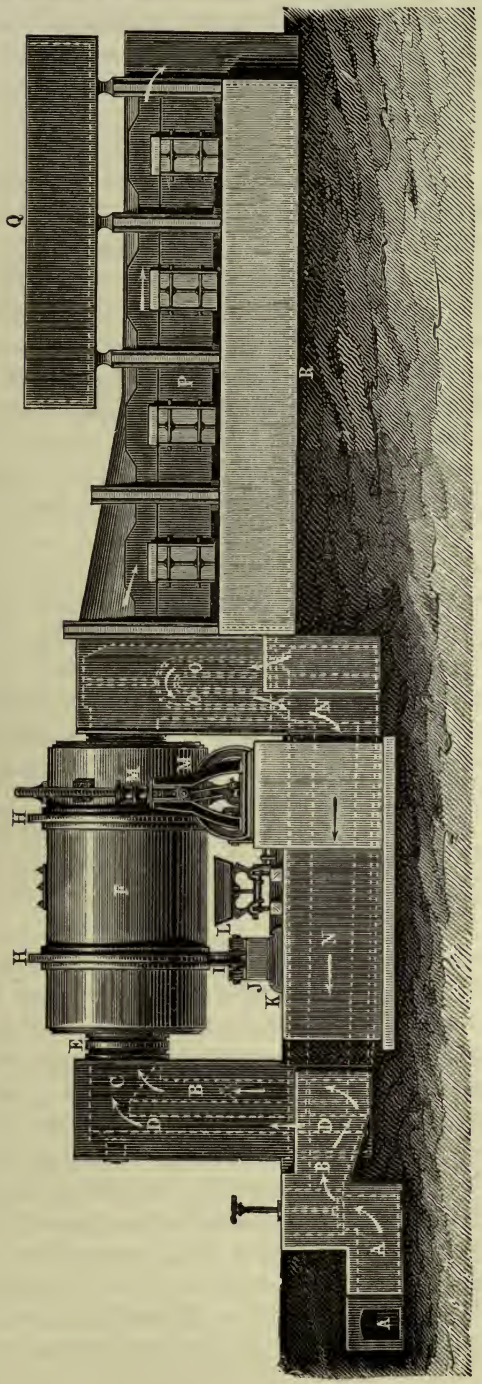


FIG. 94.

while the addition of the limestone causes the evolution of carbon monoxide to make the candle flames, and produces a limited amount of quicklime, both of which aid the subsequent lixiviation of the black-ash.

Black-ash contains as principal constituents 36 to 45 per cent. sodium carbonate, and 28 to 31 per cent. calcium sulphide; as remnants of the ingredients, 0·5 to 1·5 per cent. sodium sulphate, 1 to 7 per cent. coal, and 3 to 6 per cent. limestone; as unchanged impurities of the ingredients 1·5 to 2·5 per cent. sodium chloride, 1 to 1·5 per cent. iron as oxides, 1 to 2 per cent. aluminium silicate, 1 to 2 per cent. sand, and about 0·5 per cent. magnesia; as intentional secondary product 8 to 10 per cent. calcium oxide; as unintentional secondary products 1·5 to 2·5 per cent. sodium silicate, 0·5 to 1·5 per cent. sodium aluminate, 1 per cent. sodium ferrous sulphide, and small quantities of sodium cyanide and sodium thiocyanate from the nitrogen of the coal, also ultramarine.

153 (3) *Lixiviating the Black-ash.*—The next operation consists in the treatment of black-ash with water. The cakes are broken up, and to facilitate this they are first allowed to stand in the air for some considerable time, when they absorb water and begin to split up spontaneously. The water must be at a temperature of about 40° C., because if employed much hotter Leblanc's reaction

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

begins, though very slowly, to be reversed, that is

$$Na_2CO_3 + CaS = Na_2S + CaCO_3.$$

During lixiviation heat is evolved and the temperature rises to about 60°, and as local temperatures must be still higher, it can be understood why the black-ash liquors always contain appreciable amounts of sodium sulphide. The amount of water used must be limited in quantity so as to obtain sufficiently strong solutions; but in limiting the water the moistened black-ash must not be allowed to project through the liquor surface into the air, because it would then absorb oxygen with great rapidity; even the liquors absorb oxygen, and hence, and also because of the reversal of the reaction, the lixiviation has to be conducted as quickly as possible; the products of the oxidation are sodium polysulphides, thiosulphate, sulphite, and sulphate. A series of vats is employed in which the broken

black-ash is placed; water is allowed to flow on to that portion of the ash which by previous operations has already been nearly exhausted, and the liquor, slightly increased in specific gravity, falls to the bottom of the tank, whence it flows by a pipe to a slightly lower level in the second tank. Here and in the succeeding tanks the same actions occur, until in the last tank the strong liquor coming into contact with the fresh black-ash, is brought up to full strength, and then flows from the bottom of that tank by a pipe which rises a certain height. The height is so adjusted that a steady flow of liquor passes through all the tanks continuously; owing to the increasing specific gravity of the liquor, the liquor level in each tank adjusts itself a little lower than in the preceding tank. The final liquor has a specific gravity of about 1·3 and is always coloured. The average time needed for the lixiviation of a charge is about forty-eight hours. The residue remaining in the vats is known as alkali waste, and is described on page 301. During the lixiviation the caustic lime transforms a considerable quantity of the sodium carbonate into caustic soda:

$$CaO + Na_2CO_3 + H_2O = 2NaOH + CaCO_3.$$

Hence about one-third of the total amount of soda present in the liquor exists as caustic soda.

Besides these main constituents, the liquor contains the following impurities, the approximate quantities being given in grams per litre:

$NaCl$	Na_2SO_4	Na_2SiO_3	Na_2S	$NaAlO_2$	$Na_2S_2O_3$	Na_4FeCy_6
20	13	4·8	4	3·8	1·6	0·3

$NaSCN$	$Na_2S.FeS$
0·2	0·1.

154 (4) *Purifying the Black-ash Liquor.*—The black-ash liquor may be made to yield directly a deposit of soda crystals, but its many impurities cause the crystals to be discoloured and impure; hence many, and very various, methods have been adopted to purify the crude liquor.

(*a*) Keeping the liquors warm and allowing to settle causes a deposit of undissolved fragments from the black-ash, also of ferrous sulphide and sodium aluminium silicate.

(*b*) Acting on the liquor with carbonic acid gas, for the purpose (1) of converting the caustic soda into sodium carbonate, (2) of converting sodium sulphide into sodium carbonate with

evolution of sulphuretted hydrogen gas, (3) of decomposing the sodium ferrous sulphide into sodium carbonate and insoluble sulphide of iron, (4) of decomposing sodium silicate and sodium aluminate into sodium carbonate and insoluble silica and alumina, or compounds of the same. The carbonic acid gas was obtained from limestone and waste weak hydrochloric acid, and since that failed, from lime kilns or from the waste flue of any furnace. The gas was sometimes blown through the liquor, but more often it was passed into towers packed with coke over which the soda liquor was allowed to flow. If the gas employed contains oxygen also, that will be absorbed by the sulphides, to form polysulphides, thiosulphates, sulphites, and sulphates. This process has been in use since 1838. In 1881 the decomposition of the sodium silicate was aided by the addition of bauxite (a native hydrate of alumina).

(*c*) Acting on the liquor with air, for the purpose of converting the sodium sulphide and sodium ferrous sulphide into the various sulphur compounds just named, and ultimately into sodium sulphate and oxide of iron. This method was used in 1853 by Gossage. The action of the air was sometimes aided by adding precipitated manganese dioxide (Weldon Mud).

(*d*) Addition of zinc or zinc oxide, both of which are soluble in caustic soda solutions, to decompose the sodium sulphide, sodium ferrous sulphide and sodium ferrocyanide, with formation of insoluble zinc sulphide, iron sulphide, and zinc ferrocyanide.

(*e*) Heating the liquor to 180°C. under pressure (after it has been carbonated as above), whereby the ferrocyanides are destroyed by very complicated reactions.

After any of these treatments the liquor is allowed to settle, when the still warm and clarified liquor may be drawn off and crystallised by cooling.

Finishing the Black-ash Liquor.—The course adopted has varied much at different times and at different works, and it is regulated more by trade than by scientific requirements.

The purified liquors may be allowed to cool, and deposit washing soda crystals, $Na_2CO_3,10H_2O$, which with draining and slight washing are then ready for the market. The mother liquors, being then much more impure, are worked up by one of the following methods.

The liquors are more frequently evaporated to deposit crystals of the monohydrate, Na_2CO_3,H_2O, from the liquor while

it is still boiling, and for this purpose, the waste heat of the black-ash furnace is employed. Large iron pans, shown at D in Fig. 86, in Fig. 87 on the left side, and 89, at DD in Figs. 90 and 92, and at P in Fig. 94, are kept filled with the liquor, and as the temperature rises and the water steams off, the hydrate $Na_2CO_3,10H_2O$ ceases to exist and minute crystals of sodium carbonate monohydrate, Na_2CO_3,H_2O, deposit until the pan is filled with a thick magma of these and the mother liquor. It is on account of this thick magma of crystals that the English arrangement of setting the evaporating pans is adopted, that is, the pan is not heated from below, but the liquor is heated from above, the fire gases coming into actual contact with the liquor. The doors in the pan sides shown in the several figures are then opened, and the contents are raked out into the drainer (E in Figs. 90 and 92 and R in Fig. 94), and there allowed to drain; the mother liquor from the crystals contains largely increased amounts of caustic soda and of salt compared with the sodium carbonate, and it is either treated with sawdust and evaporated to dryness for the purpose of ultimately making a low grade ash, or else it is evaporated to dryness without any such addition to obtain ultimately a product known as "caustic ash." By special attention the monohydrate crystals may be obtained in a condition of great purity, and after well draining and slight washing they are sent into the market under the name of "crystal carbonate."

By heating the monohydrate in a reverberatory furnace it is converted into the anhydrous sodium carbonate, Na_2CO_3, commercially known as "soda ash." Monohydrate containing sodium ferrous sulphide or sodium ferrocyanide always gives an ash coloured yellow by ferric oxide.

When soda ash is to be used for cleaning wool it must be particularly free from caustic soda, but if it is to be used for soap or paper-pulp making, the presence of even a considerable amount of caustic soda is an advantage.

155 *Production of Caustic Soda from Black-ash Liquor.*— A totally different method of dealing with the caustic soda found in black-ash liquor was initiated by Gossage in 1853. Taking the mother liquor from the monohydrate crystals with its high accumulated contents of caustic soda already referred to, he continued the evaporation, but as any "salt" was deposited, whatever its nature, it was fished out with perforated ladles and so removed, until the residual caustic soda, which is the

most soluble of all the constituents of the liquor, became so concentrated that, on cooling, the whole set into a solid mass, still containing 10 to 15 per cent. water. This was the first solid caustic soda made commercially, and was known as "cream caustic"; it did not contain more than 60 per cent. alkali (Na_2O), and was blue, green, yellow, or red, but never white.

As the uses for solid caustic soda rapidly extended, the black-ash was so mixed as to yield more caustic soda in the liquor; and lastly, instead of evaporating the black-ash liquor to recover what sodium carbonate it contained, it was diluted considerably till only of about 1·09 specific gravity, and the sodium carbonate present was then causticised by adding the necessary amount of lime and heating:

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

After this the mixture was blown with air to oxidise the sulphides of sodium and iron, allowed to settle, and the liquors evaporated. During the evaporation some of the impurities, consisting of sodium sulphate and chloride, and also the small amount of sodium carbonate always remaining unacted on by the lime, crystallise and are fished out or allowed to settle; the purer liquid in the last stages of the evaporation is oxidised by a current of air or by nitre, whereby sulphides are converted into sulphate, whilst ferrocyanide is destroyed with separation of graphite, and a red precipitate of ferric oxide is thrown down. When the caustic has become anhydrous the separation of the iron is complete, as was first pointed out by Ralston in 1860, and the addition of less than a handful of nitre or of sulphur will cause a large pot holding 16 tons of molten caustic to change from yellow through white to green or *vice versâ*. After partial cooling, during which the ferric oxide settles, the still molten caustic, colourless as water, is ladled into thin sheet-iron drums. White caustic soda was first manufactured largely in 1862. By great attention to the methods of purification the caustic soda now manufactured is made to contain as much as 76 per cent. alkali, but various other strengths are made, down to 60 per cent. alkali. Sodium carbonate is no longer the principal product of the Leblanc process, but sodium hydroxide.

Alder Wright has made a series of experiments on the loss of sodium occurring in the Leblanc processes. He believes it to be as follows:—

Sodium compounds vaporised . . .	1·14 per cent.
Sodium sulphate undecomposed . .	3·49 „
Sodium compounds rendered insoluble	5·44 „
	10·07 „

156 *Alkali Waste and its Utilisation.*—The waste has a variable composition, but its nature may be seen from the following analyses, the first from a black-ash charge made for carbonate, and the second from a charge made for mixed caustic and carbonate:—

CaS.	$CaCO_3$.	Moisture.	Coke.	$Ca(OH)_2$.	$Na_2CO_3.CaCO_3,5H_2O$	Sundries.
30·17	18·53	33·79	8·46	1·22	4·01	4 51
26·46	22·26	32·98	3·84	6·33	5·63	3·31

The double carbonate of sodium and calcium occurs native as Gay-Lussite in certain Salt Lake deposits, and this compound is the cause of the loss from sodium compounds rendered insoluble. To avoid its formation the amount of lime in the black-ash charge is reduced to a minimum.

For every ton of soda-ash there are one and a half to two tons of waste produced, and this accumulates in enormous quantities.

The present method of utilising alkali waste is due to Chance, who after years of experimental work at Oldbury, near Birmingham, has devised a process that has been adopted by many large English and French works. The waste gas from lime-kilns, containing about 28 per cent. carbon dioxide and 72 per cent. nitrogen, is forced by powerful pumps through a series of from four to six tall closed cylinders containing a thin creamy mixture of alkali waste and water. The first action of the gas is to convert the calcium sulphide into hydrosulphide and carbonate:

$$2CaS + H_2O + CO_2 = Ca(SH)_2 + CaCO_3.$$

The nitrogen, the only gas remaining at this stage, is sometimes allowed to escape, so as to increase the strength of the sulphuretted hydrogen ultimately obtained; 40 per cent. of the nitrogen otherwise necessarily present being thus actually eliminated. The second action of the carbon dioxide is to convert the calcium hydrosulphide into calcium carbonate and

sulphuretted hydrogen, which necessarily is admixed with the nitrogen that accompanied the carbonic acid :

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

As it is not possible to separate these two processes completely, the strongest gas obtainable contains :

H_2S.	CO_2.	N.
33·5	1·7	64·8

but if no attempt is made to separate the two processes, the resultant gas contains only 25 per cent. sulphuretted hydrogen. The residual " cream " from the carbonating towers is entirely free from sulphides, and is filtered in presses so as to obtain : (1) a clear liquid containing about 2 per cent. of sodium bicarbonate, which is used to dissolve fresh charges of black-ash, and (2) cakes of innocuous calcium carbonate. This material is usually stacked in waste heaps, though some has been used in the making up of the black-ash charge, and some for making Portland cement.

The second part of the Chance process consists in so burning the sulphuretted hydrogen as to produce sulphur and water :

$$2H_2S + O_2 = 2S + 2H_2O.$$

Since the air used in burning the sulphuretted hydrogen contains about four-fifths its volume of nitrogen, it is clear that, start even with the strongest gas obtainable (see above), the proportion of nitrogen to sulphuretted hydrogen in the mixture submitted to combustion will be at least 4 : 1 by volume. The combustion is carried on continuously in a kiln, called the Claus kiln, lined with fire bricks, and provided with a false bottom, on which rests a layer of broken brick, and then a thinner layer of oxide of iron, which acts as a catalytic agent. and enables the reaction to proceed. The gas and air are led, each in carefully regulated quantity, under the false bottom, where they are kindled ; the heat evolved by the reaction maintains the necessary temperature of the kiln. A portion of the sulphur runs molten from the kiln, the rest distils off with the water, and by passing the vapours through cooling chambers the sulphur is condensed, partly in the molten form, and partly in the form of " flowers." If the kiln is made to do too large an amount of work, its temperature rises higher, and a new reaction sets in :

$$3S + 2H_2O = SO_2 + 2H_2S,$$

which leads to a loss of about 12 per cent. of the sulphur in the exit gases.

In practice not only do the exit gases from the Claus kiln always contain small but appreciable quantities of sulphuretted hydrogen and sulphur dioxide, but the waste nitrogen from the carbonating towers is liable to contain sufficient sulphuretted hydrogen to create a nuisance, if the carbonators are worked so as to produce a strong sulphuretted hydrogen. These drawbacks have been overcome by burning the small amount of sulphuretted hydrogen to sulphur dioxide, and either absorbing this and the sulphur dioxide originally present in a tower containing limestone and water, and running the resultant weak acid calcium sulphite to waste, or utilising the sulphur dioxide for the production of sulphuric acid.

Cryolite Process.

157 Cryolite, or sodium aluminium fluoride, $3NaF,AlF_3$, a mineral mined only in Greenland to the extent of 6,000 to 7,000 tons per annum, is used as the raw material for the manufacture of a limited amount of sodium carbonate.[1] The process, devised by Thomsen of Copenhagen in 1849, and first utilised on a large scale in 1854, is founded on the fact that when this mineral is heated with chalk, carbon dioxide escapes, leaving behind a mixture of calcium fluoride and sodium aluminate:

$$2(3NaF,AlF_3)+6CaCO_3=(3Na_2O,Al_2O_3)+6CaF_2+6CO_2.$$

The sodium aluminate is separated from the calcium fluoride by lixiviation and the solution carbonated with carbon dioxide. There is thus obtained a solution of sodium carbonate ready for evaporation to the crystallising point, and a granular precipitate containing 45 per cent. of alumina, 20 per cent. of sodium carbonate, and 35 per cent. of water, from which the sodium carbonate is extracted by long-continued washing with hot water.

In 1865 the monopoly for the cryolite was obtained by a firm near Pittsburg, and hardly any soda is made from it elsewhere.

[1] *Dingl. Polyt. Journal*, 1862, **166**, 441.

Ammonia-Soda Process.

158 This process consists in passing carbon dioxide into a solution of sodium chloride containing ammonia; ammonium carbonate and ultimately ammonium bicarbonate is formed, which then enters into double decomposition with the sodium chloride to form sodium bicarbonate:

$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl.$$

Sodium bicarbonate being very slightly soluble in a solution of either ammonium chloride or sodium chloride separates out, and after mechanical removal of the mother-liquor may be converted by calcining into the normal carbonate and carbon dioxide, which last is used again in the first part of the process. The mother-liquors, containing ammonium chloride and a considerable proportion of unaltered sodium chloride, are heated with lime, and the ammonia thus recovered is used again in the first part of the process. The only essential waste product is therefore a solution of calcium and sodium chlorides.

Simple as the process is from a chemical point of view, the practical difficulties, of a mechanical nature, were so great that, although the process was patented in 1838 by Dyer and Hemming, it was not until 1855 that it was first practically carried out by Schloessing and Rolland near Paris. They did not however, succeed in overcoming the numerous practical difficulties surrounding the subject, and abandoned the process in 1857. The credit of having brought the process to an economical issue belongs to Solvay, who in 1861 took out his first patent, in 1863 erected his first factory near Brussels, and, after five years of incessant work under trying circumstances, had made the apparatus sufficiently satisfactory to continue the running of the process. In 1872 he took out further patents, which made the process really successful, so that he was enabled to build a very large factory near Nancy; and in 1873 it was recognised that the Leblanc process had met with a permanent and powerful rival. In 1872 Solvay's output was only 10 tons of soda per day, but in 1888 the Solvay Syndicate Works in England were reported to make 125,000 tons, while those on the Continent made 245,000 tons, and those in America 60,000 tons, a total of 430,000 tons out of the world's total production of 900,000 tons by all processes; in 1900 the production of

ammonia-soda amounted to 900,000 tons, while the total by all processes was only 1,500,000 tons. The works started in England under Solvay's patents were those of Messrs. Mond, afterwards Brunner, Mond & Co., at Northwich; they commenced operations in 1874 and were the first works to use natural brine direct; various improvements introduced by L. Mond enabled their output to be increased from 2,500 tons in 1875 to 169,000 tons in 1892. Owing to the erection of other ammonia-soda works in this country the output of ammonia-soda steadily rose until in 1895 it reached 428,614 tons, thus exceeding the 408,173 tons produced by the Leblanc process. In 1904 the British ammonia-soda works consumed 1,703,805 tons of salt as such or in the form of brine. Many minor modifications have been introduced by numerous manufacturers, and the processes conducted in the ammonia-soda works of to-day contain many details differing from Solvay's original proposals.

The advantages of the process, over the Leblanc process, are: (1) that the cost of manufacture is less, chiefly because of the use of the brine pumped directly from the salt beds and because of the smaller amount of fuel required; (2) that it gives rise to no noxious by-products, and (3) that it yields a purer product. The disadvantages of the process are: (1) great care has to be exercised to avoid any considerable loss of ammonia, the cost of which is relatively very high; (2) the whole of the chlorine of the sodium chloride is lost, as no simple and economical process has yet been devised for recovering it from the calcium chloride on a very large scale, notwithstanding numerous attempts, some of which have been partially successful (see the Weldon-Pechiney process, Vol. I., p. 180, and Brunner Mond's process, this vol., p. 310); (3) the proportion of salt used per ton of sodium carbonate made is much greater than in the Leblanc process.

Brine, pumped direct from the mine, always contains minor constituents that cause considerable trouble. The constituents (grams per litre) contained in a typical sample are :—

$NaCl$	$CaSO_4$	$CaCl_2$	$MgCl_2$
290	4·5	2·1	0·6.

By treatment with milk of lime and subsequent settling, the magnesium chloride may be converted into calcium chloride and magnesium hydroxide, and the latter removed. By the

subsequent addition of either sodium carbonate, or of liquors containing ammonium carbonate, the bulk of the calcium salts are precipitated as calcium carbonate and this also is removed by settling. The purified brine must not be too strong, because otherwise the addition of ammonia gas would so reduce the solubility of the sodium chloride as to cause some of it to crystallise out. Whether water requires to be added or not depends upon the manner of preparing the ammonia gas, because this may bring with it larger or smaller proportions of water vapour.

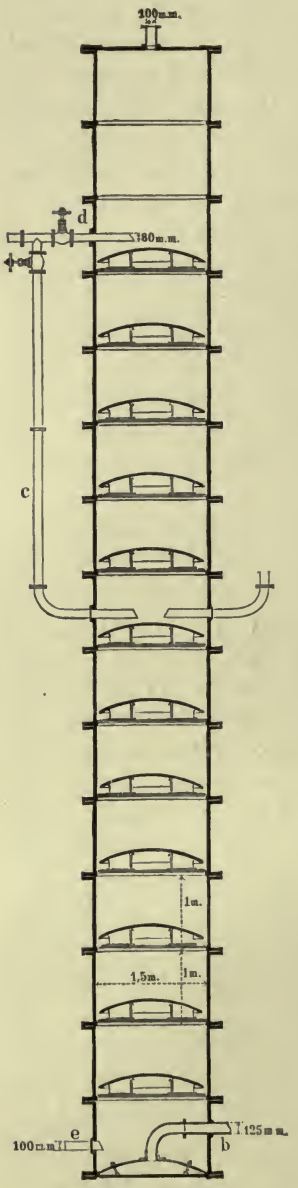


FIG. 95.

The apparatus patented by Solvay in 1872 for saturating the brine with ammonia has by a number of changes been simplified and rendered less liable to interruptions from the residues of the lime and magnesia salts just referred to. The apparatus is sometimes a simple vertical tank containing the purified brine, into the bottom of which the ammonia gas is forced by pressure generated in the still where the gas is made. Sometimes it is a tower subdivided by many partitions over which the liquor flows gradually downwards, while the ammonia gas at almost atmospheric pressure passes up the tower. Whatever the form of the apparatus, the solution becomes warm, and by various cooling devices is partially cooled. Owing to the residual lime and magnesia salts in the brine, a precipitate of the carbonates of these metals is formed, which is prevented from becoming admixed with the sodium bicarbonate subsequently formed by

passing the ammoniacal brine through a series of settling tanks, from the conical bottoms of which the mud may be drawn off. The resulting liquor, containing an average of 60 grams NH_3 and 270 grams NaCl per litre, is run into a montejus, whence it is forced by gas pressure from the carbon dioxide mains into the carbonating tower.

The form of carbonating tower introduced by Solvay is shown in Fig. 95, and consists of a large number of superposed cylindrical compartments or drums, one of which is shown on a larger scale in Fig. 96. The bottom of each compartment has a large circular opening in the centre, over which is a perforated sieve having the shape of a spherical segment, which

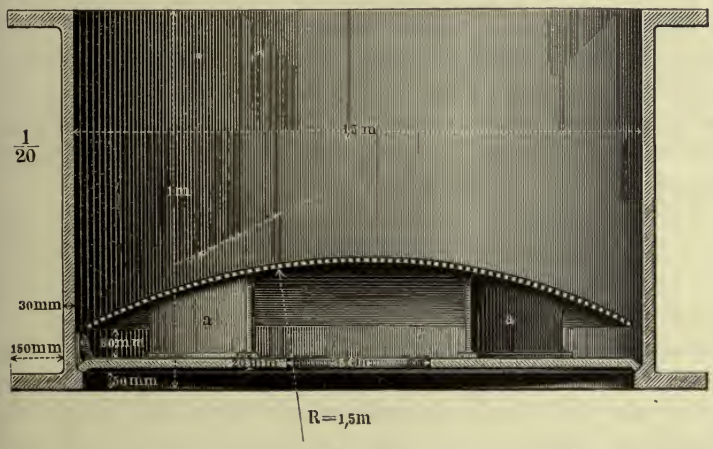


Fig. 96.

is supported by light stays and does not quite reach the inner wall of the drum. The ammoniacal brine enters some distance below the top of the tower by the pipe c, and fills the tower nearly to the top. The carbon dioxide, forced in at the bottom under a pressure of 1·5—2·5 atmospheres, is divided by the sieve holes into numerous small streams, which pass through the brine and reunite in the large central opening of the next compartment; this subdivision of the gas is repeated in each compartment. But as the holes in the Solvay tower after about a fortnight's work get plugged up with a scale of sodium bicarbonate, the process has to be stopped and the towers washed out with boiling water, and then allowed to cool.

To obviate this difficulty other forms of carbonator are used

amongst which may be mentioned that of Honigmann, viz., a set of three cylinders, through which the carbon dioxide is passed in succession at a much lower pressure than that employed by Solvay. When the contents of the first vessel are carbonated, it is discharged, refilled with fresh ammoniacal brine, and replaced in the series, but as the last vessel; the vessels are 10 feet diameter and 10 feet high only.

The carbon dioxide is obtained partly from the lime-kilns required to prepare the lime subsequently used to recover the ammonia, and in that case contains about 30 per cent. carbon dioxide, and requires cooling and freeing from accompanying dust and sulphur dioxide; this is effected by making it bubble several times through shallow layers of flowing water. Carbon dioxide is also obtained from the calcination in closed pans of the sodium bicarbonate, and is then much purer than the above (see next page). The gas is drawn by a powerful pump, and delivered at a pressure of about 45 lb. per square inch for the Solvay towers, or 10 lb. for the Honigmann apparatus.

The absorption of the carbon dioxide to form first normal ammonium carbonate, $(NH_4)_2CO_3$, and then the bicarbonate, $(NH_4)HCO_3$, is accompanied by the evolution of a considerable amount of heat which is removed by a series of horizontal water-cooling tubes passing through the Solvay tower, or by flowing cooling water over the exterior of the Honigmann carbonators. In no case may the temperature exceed 70°, or the ammonium carbonates begin to decompose; neither may the temperature be lowered too much, because then the sodium bicarbonate comes down so finely divided that it is most difficult to filter and wash, and at 10° ammonium chloride begins to crystallise out. During the reaction the temperature should be kept at 30—40°, but just at the last it may be reduced to 15°, to render the separation of the sodium bicarbonate more complete.

The inert gases escaping from the carbonating apparatus always carry away about 8 per cent. of the total ammonia originally present in the ammoniacal brine; to recover this the gases are passed through a series of scrubbers, some containing brine, others water, and others dilute sulphuric acid.

Every half-hour a portion of the contents of a Solvay tower is drawn off from the bottom of the tower, or at suitable intervals one of the Honigmann carbonators is blown empty by compressed gas. The pasty liquid runs on to vacuum filters,

which retain the crystals of sodium bicarbonate; the latter is washed very carefully with water to remove the ammoniacal mother liquor as completely as possible, and in doing this approximately 10 per cent. of the bicarbonate is lost.

The washed bicarbonate is dried and calcined, by which treatment the small quantity of accompanying ammonium salts is decomposed with liberation of free ammonia, and about three-quarters of the bicarbonate is converted into sodium carbonate, carbon dioxide, and steam. Many different forms of apparatus have been patented by Solvay and others for conducting this operation; that known as a Thelen pan is largely used. It consists of a semi-cylindrical cast-iron pan heated externally from below, and provided with a central shaft having an oscillating or rotary motion; to the shaft are fixed arms carrying pivoted shovels, which push the encrusted carbonate off the pan sides and gradually move it from end to end, so that it is discharged of uniform quality. The pan is suitably covered, so that the evolved gases may be sucked away; they are cooled, then passed through a scrubber to recover the ammonia, and are lastly forced by a special pump into the carbonating apparatus; if due care is taken in working the apparatus, the gases may contain 60—80 per cent. of carbon dioxide.

The resulting sodium carbonate may for some purposes be used as it is, but for others it is necessary to heat it more strongly, to decompose all the bicarbonate and to make it less voluminous for packing and shipping. This second heating is done in reverberatory furnaces fired by coke, and no use is made of the carbon dioxide in the resulting gases. The hot product is cooled on iron plates, and then packed in casks or bags.

The mother-liquor from the sodium bicarbonate contains approximately one-third of the original salt unaltered; and in place of the salt actually decomposed it contains the corresponding amount of ammonium chloride, and in addition an excess of ammonium bicarbonate equal to about one-fifth of the ammonium chloride present. The treatment of the mother-liquor consists first in simple heating, which decomposes almost all the ammonium bicarbonate. The resultant gases, carbon dioxide and ammonia, are separated from the bulk of the accompanying steam by the use of a distilling column, and are then both utilised by being absorbed by fresh brine in the ammonia apparatus. To the residual hot liquid containing the sodium and ammonium chlorides a sufficiency of lime is

added, and the treatment with steam continued until the gases evolved, which are drawn off by an air pump, are practically free from ammonia. The efficient recovery of the ammonia at this stage, and also at the minor stages previously described, is the criterion for the commercial success of the whole manufacture, for the preparation in one operation of one ton of "ammonia ash," valued at £4, requires the assistance of the ammonia obtained from no less than two and a half tons of ammonium sulphate, valued at £32. The efficiency of the recovery has been constantly improved, until now in well-conducted works it is well over 99 per cent.

The waste liquor from the ammonia stills, with considerable quantities of suspended calcium carbonate and hydroxide, is run into settling tanks to deposit the solids, which are waste, and the clear liquor, containing the undecomposed salt, and calcium chloride corresponding to the decomposed salt, is run into the water-courses also to waste. The whole of the chlorine in all the salt employed is thus lost, and many attempts have been made to recover either the sodium chloride or the chlorine of the calcium chloride, but without any permanent success. The latest method has been worked out by Messrs. Brunner, Mond & Co., at Northwich, and is characterised by bringing in an additional product, namely, zinc. The waste liquor is treated with carbon dioxide and a crude form of zinc oxide, such as roasted zinc blende, or with crude zinc carbonate, as calamine, when one of the following reactions occurs:

$$CaCl_2 + ZnO + CO_2 = ZnCl_2 + CaCO_3,$$
$$CaCl_2 + ZnCO_3 = ZnCl_2 + CaCO_3.$$

The liquor is filtered, and the solution of zinc chloride (containing of course the sodium chloride originally present) is purified and then electrolysed with carbon anodes, the products being chlorine gas, which is absorbed in slaked lime to make bleaching powder, and metallic zinc (at the cathode) almost chemically pure and having an exceptional value for making alloys. The daily output of bleaching powder from this source was nine tons in 1901. During the purification of the crude zinc chloride solution the cadmium contained in the zinc ore is isolated.

In recent years the ammonia-soda works have not been content to send out their alkali in the form of soda-ash only, for they now convert the same into soda crystals, by solution in warm water and crystallisation by cooling, or into caustic soda,

by the ferric oxide process (see p. 317) or by the old method of dissolving in boiling water and agitating with lime. The liquor produced in either of these ways being quite free from sulphides is not so corrosive towards iron, and therefore it is no longer necessary to adhere to the simple forms of evaporators—thick cast iron pans—which are so usual in alkali works. The first economy in evaporating caustic soda solutions was to conduct the first part of the evaporation in steam boilers, and to utilise the steam for any desired purpose; but the liquor proved to be too corrosive. A steam-heated multiple-effect vacuum apparatus known as the Yanyan was next tried, followed in 1888 by other forms of similar apparatus. In 1902, an improved form was introduced by Kestner which has been successfully applied very widely to ammonia soda-ash liquors on the Continent, and a little later to Leblanc caustic liquors in this country. The economy in fuel effected by this so-called multiple-effect apparatus is very considerable; the apparatus is termed a climbing film one, because the liquor while undergoing evaporation exists only as a very thin film on the sides of the long vertical heating tubes up which it is driven by the violent rush of the steam evolved from itself. The liquor contains 77 per cent. caustic soda.

Electrolytic Processes.

159 Although the electrolytic decomposition of common salt solution with the production of caustic soda was noticed by Cruickshank in 1800, and although the quantitative relations of such electrolysis were made known by Faraday, who also showed how to convert mechanical into electrical energy, yet it was not until 1872, after Gramme in Belgium had built the first useful dynamo, that electrochemical processes other than the deposition of thin coatings of copper, silver, gold, and nickel, became commercially possible.

The first electrochemical process on a large scale was that of copper refining, started in 1876; this was followed in 1883 by the work of Höpfner in Duisberg for the electrolysis of potassium chloride solutions.

Höpfner placed the anode at the top of the solution so as to allow of the ready escape of the chlorine, and the cathode at the bottom, and stopped the evolution of hydrogen at the cathode, which would otherwise disturb the dense layer of caustic potash

solution forming on the cathode, by covering the cathode with copper oxide which was reduced to metallic copper while the hydrogen was oxidised to water. When the copper layer became inert, it was removed, and exposed to the air, whereby it was reconverted into copper oxide, and was then utilised again in the process. Trials in Duisberg and other places showed that the process was not satisfactory.

In 1885 a new process had been worked out at Duisberg and an experimental works was erected in Griesheim. The separation of the products of the electrolysis was here effected by a porous diaphragm made from Portland cement mixed with acidified brine; the shape of the diaphragm was that of a box, through the lid of which the carbon anode passed. After the complete setting of the cement, a soaking in water removed the crystallised salt and the lime salts produced by the added acid, and the diaphragm was thus made very porous so as to permit an easy passage of the electric current. A number of such porous vessels with anodes were placed in an outer vessel, with a cathode between every pair of anodes. The vessels were filled with potassium chloride solution, and the same solid salt was fed into the anode vessel to keep that liquor saturated. On passing the electric current, chlorine is evolved at the carbon anodes and thence passes away by suitable pipes, while the potassium is liberated at the cathodes and reacts there with the water to form caustic potash and hydrogen. When the caustic has increased to 40–80 grams per litre of the cathode liquor, the liquor is removed and evaporated in multiple-effect vacuum evaporators so arranged as to allow of the removal of the large quantity of undecomposed potassium chloride which separates; the concentrated mother-liquor is then further evaporated to produce the solid alkali. The current efficiency is only 70–80 per cent. The carbons are quickly attacked, and the escaping chlorine contains 5–8 per cent. of carbon dioxide. The porous diaphragms do not completely prevent the cathode liquor from obtaining access to the anode, hence hypochlorites and chlorates are formed in the anode liquor and oxygen is evolved at the anode, so that the escaping chlorine may contain 10 per cent. of electrolytic oxygen.

More resistant electrodes are now made of cast magnetite prepared thus; burnt pyrites, from the manufacture of sulphuric acid, is heated in an electric furnace to fusion; the Fe_2O_3 is thus converted into FeO, and therefore further quantities of Fe_2O_3

are added just before casting into the anode forms, so as to bring the melt to the composition Fe_3O_4.

This Griesheim "Elektron" process, in spite of its many imperfections, is so successful that in 1912, at works in Griesheim, Bitterfeld, Westeregeln, Ludwigshafen, and Rheinfelden in Germany, at Lamotte in France, at Flix in Spain, and at works in South Russia, no less than 33,000 horse power were being employed.

In England there is no native potassium chloride to convert into caustic potash, and the pecuniary inducements to electrolyse sodium chloride were not nearly so great. The first serious attempts were not made till 1888, when at the Snodland Paper Works in Kent the process of Greenwood was tried. In this a diaphragm built up of alternate layers of porcelain rings and asbestos is utilised. The caustic liquid produced contained but 2·2 per cent. of caustic soda and this was accompanied by 10·7 per cent. of sodium chloride.

A process of Richardson and Holland was next tried, in 1890. No diaphragm was used; the cathode was covered with oxide of copper as in Höpfner's process already described, and in this country also the process was a failure.

In 1892 Hargreaves and Bird introduced a novelty in that the cathode, instead of being separate from the diaphragm, is so completely adjacent to it that the two are built up together, and the liquor which percolates from the anode compartment through the diaphragm hangs upon the iron wire gauze forming the cathode by capillary attraction only, and the cathode compartment contains no other liquor. From the cathode the alkali is washed away by passing steam into the cathode compartment. The efficiency of the cell is increased by bringing into the cathode compartment waste gases containing carbon dioxide, but the product is thereby changed from caustic soda to sodium carbonate, which is obtained as crystals $Na_2CO_3,10H_2O$. This process is worked with the Cheshire brine at Middlewich.

In 1892 Castner in Oldbury, near Birmingham, and Kellner in Vienna began to electrolyse brine in a fundamentally different manner. In all the foregoing and also in all the subsequent processes it is to be noted that great difficulties are encountered in the endeavour to separate completely the products of two reactions:

$$2NaCl = Na_2 + Cl_2, \text{ and } Na_2 + 2H_2O = 2NaOH + H_2,$$

and in none of these electrolytic processes above-mentioned is this complete separation obtained; by that next described the separation is obtained. In 1807 Davy discovered sodium amalgam; in 1882 and succeeding years proposals were made to use it in the electrolysis of brine. Of these, the processes of Castner and of Kellner in 1892 have proved successful.

The anodes are arranged in the upper part of the brine, and at the bottom of the latter is a moving layer of mercury which forms the cathode. When the electric current is made to pass, chlorine gas is evolved at the anodes and rising through the brine passes out from the apparatus by a suitable pipe. The sodium liberated at the cathode unites there with the mercury to form sodium amalgam, which rapidly diffuses from the surface into the mass of the mercury below. Whilst sodium is acted upon with great rapidity by water, with sodium amalgam the reaction takes place much more slowly, and therefore it is easily possible to remove the sodium amalgam from the apparatus. The sodium amalgam passes into an adjacent cell or compartment which is fed with water and contains also a solid electrode; these three items form the elements of a galvanic battery and as soon as the circuit is closed the water or the dilute caustic soda solution is electrolysed, hydrogen being evolved on the upper solid electrode and oxygen being evolved on the amalgam, which thus loses its sodium, and the strength of the caustic soda solution is increased. Finally the mercury is returned to the first compartment or cell and the operations are repeated. The two essential reactions are thus absolutely separated, and the caustic soda solution obtained is very much stronger and purer than can be obtained by any of the preceding or succeeding processes. Mercury processes are used at Weston Point, Cheshire, at Bernburg, Osternienburg, and Rheinfelden in Germany, at Jemeppe in Belgium, and at Niagara Falls in the United States.

In 1898 a modified form of a process originally devised by Richardson and Holland was worked out at Aussig in Austria with certain modifications. Into the upper part of a bell-jar is fixed an anode, and also an inlet for a constant small supply of brine; twenty-five of these bells stand in a large bath that contains the cathodes. By very careful attention to the various dimensions, the current density, and above all to the feed of the fresh brine into the upper part of the bell, and the removal of the caustic liquors from the outer

cell, this process with its simple apparatus has been made to yield good results. A large portion of the improvement over the original process of Richardson and Holland is attributed to the counterflow movement between the constant brine feed and the electrolytic migration of the hydroxyl ions from the cathode to the anode. In 1912, works in Austria and in Germany were utilising 6,000 horse power.

A similar counterflow movement of brine and hydroxyl ions occurs in the Hargreaves-Bird cell already described, but the movement of the brine through the diaphragm is irregular owing to the varying hydrostatic head.

In 1905 Townsend introduced at Niagara Falls and at Sault St.-Marie in the United States a cell very similar to that of Hargreaves and Bird with a more complete counterflow movement. The improvement is made by filling with paraffin oil that part of the cathode chamber which in the Hargreaves-Bird cell is full only of steam and waste combustion gases. The hydrostatic heads of the brine and of the oil may be made nearly to balance, and by regulating the outlet level of the brine the percolation of the brine through the diaphragm to the cathode can be controlled and the percentages of caustic and salt in the product kept at any desired figures. The hydrogen bubbles and the alkaline liquor are constantly thrown off from the cathode into the body of paraffin oil; the hydrogen rises to the surface of the oil, whilst the liquor sinks to the bottom and is then drawn off by an inverted syphon.

In 1906 the principle of the counterflow of an electrolyte and the migration of an ion was embodied in a cell designed by Billiter. This cell contains only a shallow horizontal layer of alkali cathode liquor just sufficient to immerse the iron gauze cathode. The gauze cathode forms the bottom of the anode cell, and upon it rests an asbestos cloth and then a layer of precipitated barium sulphate which thus forms a diaphragm. To facilitate the escape of the hydrogen from the cathode, the latter is made slightly inclined and corrugated. The anode chamber is nearly full of brine, and by regulating the same the amount slowly passing through the barium sulphate layer to the cathode is also regulated.[1] In 1912 these cells working in Germany, Austria, and the United States utilised 6,000 horse power.

In 1906 the same principle was carried to its limit by

[1] Compare Allmand, *Trans. Faraday Soc.*, Nov. 1912.

Finlay who adopted the principle for both the anion and the cation. He divided a cell by two diaphragms into three compartments; into the middle or second of these he fed brine, which then passed in two opposite directions through the diaphragms, to the anode in the first compartment, and to the cathode in the third compartment. When making a liquor containing 8 per cent. caustic soda, the current efficiency is said to be as high as 98 to 99 per cent.

The magnitude of the total alkali chloride electrolytic process is now (1912) such that the horse power employed is 70,000. A general account is found in Lunge's *Alkali Manufacture*, Vol. 3, an account of the scientific principles in Allmand's *Electrochemistry* (1912), and details of apparatus, and of patents in the several volumes of *Monographien über angewandte Elektrochemie* as follows: Vol. 41:—The electrolytic decomposition of alkali chlorides with solid metal cathodes, by Billiter (1912): Vol. 23:—The same with liquid metallic cathodes, by Lucion (1906); Vols. 24, 29, 32 and 33:—The electro-chemical patents of Germany (1906), of England (1908), and of America (1910), by Ferchand; Vol. 12:—The electro-chemical industries of Germany, by Ferchand (1904); and Vol. 28:—The electro-chemical and electro-metallurgical industries of Great Britain by Kershaw (1907).

Commercial Forms of Alkali.

160 *Soda Crystals.*—For household use, there is a considerable demand for the soda in the crystalline form containing 10 molecules of water. This is prepared by the direct Leblanc method (p. 298), or by dissolving calcined soda ash in hot water, allowing the impurities to settle, and then running the clear liquor into crystallising tanks (p. 301).

Crystal Carbonate.—The monohydrated carbonate Na_2CO_3,H_2O, known as "crystal carbonate," has the advantage over soda crystals that it contains a larger percentage of alkali, and dissolves much more readily in water, and that with a slight evolution of heat.

Sodium Bicarbonate, $NaHCO_3$, is used in medicine, and for preparing aërated waters, and for baking powders. It was fomerly manufactured on a large scale by exposing soda crystals enclosed in large chambers to carbon dioxide generated by the action on limestone of the dilute and otherwise waste hydrochloric acid obtained in the Leblanc soda process. The gas was slowly

absorbed by the crystals, which lost their transparency, and then their water of crystallisation:

$$Na_2CO_3,10H_2O + CO_2 = 2NaHCO_3,9H_2O.$$

The large quantity of water liberated dissolved and washed away the greater part of the impurities present in the soda crystals, and when the flow of liquor ceased the reaction was complete; the wet bicarbonate was dried at a very gentle heat.

In 1882 Carey, Gaskell, and Hurter introduced a cheaper method of manufacture by treating crystal carbonate, Na_2CO_3,H_2O, with pure carbonic acid in a revolving cylinder, and so obtaining a bicarbonate of greater purity, corresponding to the greater purity of the raw material. A still cheaper process is now used, the bicarbonate produced as first product in the ammonia-soda process being purified from the accompanying ammonium chloride by recrystallisation from warm water (Mond, 1884), or by heating in an atmosphere of carbon dioxide to drive off the ammonia.

Sodium Sesquicarbonate. — This form of alkali was first manufactured in 1886 by Watts and Richards. The salt has the composition $Na_2CO_3,NaHCO_3,2H_2O$, and is obtained by mixing the ingredients in aqueous solution and allowing them to crystallise above 35°. The salt is permanent in the air, is readily soluble in water, and finds application in wool washing.

Caustic Soda.—The methods employed by the Leblanc Alkali Works for the manufacture of caustic soda have already been described. The ammonia-soda works also manufacture caustic soda, and the quality obtained is better; it tests 77 per cent. alkali (Na_2O).

Another method of converting sodium carbonate into caustic soda was introduced by Löwig in 1882. The carbonate mixed with ferric oxide is heated to bright redness, when carbon dioxide is evolved, and a compound of Na_2O and Fe_2O_3 is formed, called sodium ferrite; by treating this with cold water certain impurities may be washed out, and the compound is then decomposed by treatment with a small quantity of nearly boiling water, when the ferric oxide is regenerated ready for the next operation, and a very strong solution, viz., about 30 per cent. caustic soda, is formed.

The Castner electrolytic process produces a strong solution of caustic soda directly as already described, and by evaporation

and fusion it yields at once caustic soda of the highest purity attainable.

Caustic soda, besides being manufactured in the solid form of various grades of purity so as to test 60, 70, 74, 76, 78 per cent. alkali (Na_2O), is also made in the form of a strong solution of 1·45 specific gravity, containing 41 per cent. caustic soda.

Caustic soda is used for making hard soap, for disintegrating vegetable materials to obtain the fibre for papermaking, for bleaching cotton, for extracting creosote oils, purifying paraffin oils, manufacturing oxalic acid, alizarin and sodium, and many other purposes.

POTASSIUM. K = 39·10.

161 The discovery of this metal is described as follows by Davy.[1] "A small piece of pure potash which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4, in a state of intense activity; and a platina wire, communicating with the positive side, was brought in contact with the upper surface of the alkali. The whole apparatus was in the open atmosphere.

"Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrisation. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid, but small globules having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces. These globules, numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle the basis of potash. I found that the platina was in no way connected with the result, except as the medium for exhibiting the electrical powers of decomposition, and a substance of the same kind was produced when pieces of copper, silver, gold, plumbago, or even charcoal were employed for completing the circuit.

[1] *Phil. Trans.*, 1808, **98**, 4.

"The phenomenon was independent of the presence of air, I found that it took place when the alkali was in the vacuum of an exhausted receiver."

To this metal Davy gave the name of potassium. Soon after Davy's discovery, Gay-Lussac and Thénard[1] showed that the metal might be obtained in greater quantity by decomposing potash by means of metallic iron at a white heat. For this purpose iron turnings or wire were heated to whiteness in a gun-barrel covered with clay, and melted potash allowed to pass slowly over the ignited iron. The iron took up the oxygen of the hydroxide, whilst potassium and hydrogen were set free. The potassium passed over in the state of vapour, and was condensed in a copper vessel containing naphtha. A still better method was suggested by Curadau,[2] which consisted in the decomposition of the potash by means of charcoal at a white heat.

Davy's discovery of the compound nature of the alkalis attracted universal attention, and chemists throughout Europe were occupied with a repetition of his experiments, and an examination of the remarkable properties of the singular metals which can thus be obtained. So singular indeed were these properties, that many chemists denied to these substances the name of metal, and by some they were considered to be compounds of hydrogen, this view being apparently borne out by the evolution of hydrogen when these metals were thrown into water. A more accurate examination, however, of the properties of these substances proved them to be of a truly metallic nature.

Sources of Potassium.—Potassium is found in nature, in a state of combination, widely distributed. It occurs as a constituent of many silicates, forming from 1·7 to 3·1 per cent. of the granite composing the earth's solid crust. Amongst the silicates which contain potash as an essential constituent may be mentioned potash felspar or orthoclase, leucite, and analcite. Pure chloride of potassium or *sylvine*, KCl, is found in considerable deposits, together with *carnallite*, $KCl,MgCl_2,6H_2O$, in the neighbourhood of Stassfurt in Germany; it is found also in considerable quantities in Searles Lake, California. This same salt and other potash compounds occur in small quantity in the water of the ocean, and in that of many lakes such as the Dead Sea, as well as in mineral waters and in ordinary spring water.

[1] *Ann. Chim.*, 1808, **65**, 325. [2] *Ibid.*, 1808, **66**, 97.

Chloride of potassium is found also in cubic crystals surrounding the fumeroles of Vesuvius. All fruitful soil contains potassium compounds, derived from the gradual disintegration of the above-mentioned silicates. These are taken up by the rootlets of the plant, as no vegetable growth can flourish without this substance. It has been shown by Way that soil possesses the power of absorbing potash salts, whilst soda salts pass through it unabsorbed. The form in which the potash is contained in most soils is that of a salt of an organic acid, and this becomes converted into carbonate by ignition.

The potash which sheep draw from the land is excreted in large quantity from the skin in the sweat, termed by the French *suint*. No less than one-third of the weight of raw merino wool consists of this material.

162 *Preparation of Metallic Potassium.*—The method first proposed by Curadau, and brought into a practical form by Brunner, was much improved by Wöhler, and especially by Donny and Mareska.[1] This process depends upon the fact that at a white heat carbon reduces potassium carbonate, as follows:

$$K_2CO_3 + 2C = 2K + 3CO.$$

An intimate mixture of charcoal and potassium carbonate is obtained by igniting crude tartar (acid potassium tartrate) in a covered iron crucible; the porous mass is rapidly cooled by dipping the crucible into cold water, and the charred mass introduced into an iron bottle. It has been usual to place the mixture in a wrought-iron mercury bottle, connected with a copper receiver by a short iron tube.

In the preparation of the metal potassium, according to Brunner's original method, serious explosions sometimes occurred, owing to the fact that at a very high temperature the metallic potassium unites with the carbon monoxide generated at the same time to form a black compound, $K_6C_6O_6$, which is excessively explosive. By rapidly cooling the vapour of the potassium as it is produced, the formation of this compound may be prevented. This rapid cooling of the vapour is effected by using the condenser, first suggested by Mareska and Donny, shown in Fig. 97. It consists of two pieces of cast iron *d s*, which can be clamped together so as to form a shallow box about a quarter of an inch deep, ten to twelve inches long, and four to five inches in width. The socket at

[1] *Ann. Chim. Phys.*, 1852 (3), **35**, 147.

the one end fits on to the short tube placed in the neck of the bottle, or at the closed end of the retort, whilst the open end permits a free passage to the gases or vapours given off in the reaction. The object of this flattened condenser is to ensure the rapid cooling of the vapour of the metal, and thus to prevent the formation of the explosive compound with carbon monoxide. The above-mentioned reduction takes place only at a white heat, and hence it is necessary to prevent the oxidation of the iron of the retort by covering it with a coating of fire-clay. As soon as this temperature is reached the vapour of the metal begins to appear at the open end of the tube. The receiver is then adjusted to the end of the tube as shown in Fig. 98, and the metal

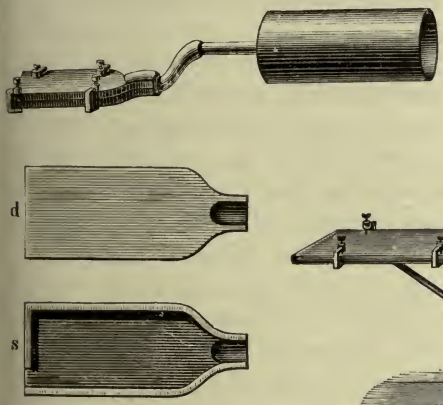


Fig. 97.

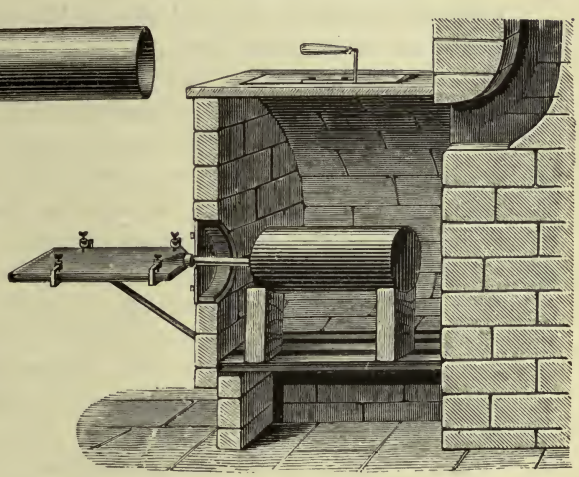


Fig. 98.

begins to condense and drops out in the liquid state into a vessel filled with rock-oil placed beneath the receiver, which does not require to be artificially cooled. Should any deposit or obstruction occur in the tube, this must at once be removed by a red-hot rod thrust into it. It is found in practice that about half the theoretical quantity of metal is obtained.

Potassium can be prepared on the small scale by the electrolysis of potassium cyanide. This salt is melted and then allowed to cool, so that a solid crust is formed; a current from three or four accumulators is then allowed to pass through the molten salt from electrodes made of gas carbon.[1]

A better method of obtaining potassium on the small scale by

[1] Linnemann, *J. pr. Chem.*, 1858, **73**, 413.

electrolysis is that proposed by Matthiessen.[1] For this purpose a mixture of potassium chloride and calcium chloride in molecular proportions, which melts at a much lower temperature than potassium chloride alone, is fused in a small porcelain crucible over a lamp, two carbon poles connected with six to eight Bunsen's elements being dipped into the fused salt. The flame of the lamp is then so adjusted that the portion of salt around the negative pole becomes solid, whilst around the positive pole the mixture is liquid, thus allowing the free escape of the chlorine. After the current has passed through for about twenty minutes in this way the crucible is allowed to cool, and opened under rock-oil, when a considerable quantity of pure potassium is found around the negative pole, no calcium being deposited.

A modification of the Castner process for the manufacture of sodium (p. 240) can be employed. On electrolysing fused potassium hydroxide the metal spreads throughout the electrolyte as a mist and becomes oxidised at the anode. If, however, the cathode is protected by a closed inverted cylinder of magnesite, the metal can be readily collected and when prepared by this method is particularly pure.[2] There is, however, at present no great demand for metallic potassium, as the cheaper sodium is equally applicable for almost all purposes, and moreover, owing to the difference in their atomic weights, 23 parts of sodium are equivalent to 39 parts of potassium.

163 *Properties.*—Potassium is a silvery-white lustrous metal with a bluish tinge, having a specific gravity of 0·875 at 13° (Baumhauer),[3] and it is therefore lighter than all other metals, with the single exception of lithium. It is brittle at 0° and possesses a crystalline fracture; at 15° it becomes soft like wax, and may be easily cut with a knife, and the two clean surfaces of the metal may be welded together like red-hot iron. It melts at 62·5°(Bunsen), forming a liquid closely resembling mercury in its appearance. Potassium may be easily obtained in the crystalline form. For this purpose some of the metal is melted in a glass tube filled with coal-gas; as soon as the mass begins to solidify the tube is quickly turned round and the portion of metal still remaining liquid is poured off from the crystals;

[1] *Journ. Chem. Soc.*, 1856, 30.
[2] Lorenz and Clark, *Zeit. Elektrochem.*, 1903, **9**, 269
[3] *Ber.*, 1873, **6**, 655.

these form tetragonal octahedra having a greenish-blue colour.[1] It has been obtained in the form of a bluish-violet colloidal solution in ether by the electrical method (p. 73).[2]

Potassium boils at 757·5°,[3] and emits a beautiful green-coloured vapour exhibiting a characteristic channelled-space absorption spectrum (Roscoe and Schuster). The green colour of potassium vapour can be readily shown by evaporating a small portion of the metal contained in a wide glass tube three dcm. in length through which a current of dry hydrogen gas is passed. On heating the metal, the tube becomes filled with splendid green-coloured vapour, condensing on the cooler parts of the tube in the form of a bright metallic mirror. When the hydrogen which issues from the end of the tube is lighted, the flame is tinged with the violet colour characteristic of potassium. Next to cæsium and rubidium, potassium is the most electro-positive metal, and it is a good conductor of electricity. In perfectly dry and pure air it does not undergo any change, but in ordinary air the clean surface of the metal soon becomes converted into caustic potash and potassium carbonate. The oxidation of a newly-cut surface of potassium in the dark is attended with luminosity (Baumhauer). Oxidation takes place so quickly when the metal is exposed to the air in thin layers that sometimes ignition occurs and the metal burns with its characteristic violet flame. When heated in the air to its point of volatilisation, it at once bursts into flame, but if the burning metal is plunged into perfectly dry air or oxygen the flame is immediately extinguished.

When thrown upon water, potassium decomposes the water with great vigour, sufficient heat being generated to ignite the hydrogen which is evolved, and which burns with the violet potassium flame. The molten globule swims about, being separated by a layer of steam from the surface of the water, and becomes gradually smaller, leaving at last a globule of fused potash, which causes an explosive burst as soon as its temperature sinks low enough to allow it to come actually in contact with the water.

Potassium acts as a powerful reducing agent, and hence it has been employed for the preparation of such substances as

[1] Long, *Journ. Chem. Soc.*, 1861, **13**, 122.

[2] Svedberg, *Ber.*, 1905, **38**, 3616.

[3] Ruff and Johannsen, *Ber.*, 1905, **38**, 3601; compare Perman, *Journ. Chem. Soc.*, 1889, **55**, 326.

boron and silicon from their oxides, and magnesium, aluminium, and other metals from their chlorides. Potassium also decomposes nearly all gases which contain oxygen, and hence it is used in some cases to ascertain the composition of gases.

Sodium forms with potassium an alloy which is liquid at the ordinary temperature, and looks like mercury. When it contains 16 parts of potassium to 10 parts of sodium this alloy becomes pasty at 8°, and solidifies at lower temperatures. If more potassium is contained in it, the alloy remains liquid below 0°. The alloy is obtained not only by melting the two metals together under rock-oil, but also by adding sodium to fused acetate of potassium when gases are rapidly evolved and the alloy formed (Wanklyn). It is also formed when caustic potash is heated with sodium, and burns in the air, forming a mixture of the peroxides of sodium and potassium; this is used under the name of "pneumatogen" for the regeneration of expired air in life-saving apparatus.[1]

COMPOUNDS OF POTASSIUM.

Potassium and Oxygen.

164 Potassium forms only two well-defined oxides, namely, potassium monoxide, K_2O, and potassium peroxide, K_2O_4. The first of these corresponds to the stable monovalent potassium salts, and combines with water to form the hydroxide. The higher oxide does not yield corresponding salts, but behaves as a peroxide. In addition to these, oxides of the formulæ K_4O, K_8O_5, K_6O_4, K_4O_3 and K_2O_2 have been described, but their existence is doubtful.

Potassium Monoxide, K_2O.—When the mixture of oxides obtained by burning potassium in slightly moist air is strongly heated, it loses oxygen and leaves a residue of the monoxide, which may also be prepared by heating caustic potash with potassium:

$$2KOH + 2K = 2K_2O + H_2.$$

It is usually prepared by melting potassium and, without furthur application of heat, leading the requisite volume of pure

[1] For other alloys of potassium consult Smith, *Zeit. anorg. Chem.*, 1907, **56**, 109.

and almost dry air over it.[1] According to Holt and Sims,[2] the product always contains metallic potassium, but it has been prepared pure by Rengade by distilling off the metal in vacuum.[3]

The pure oxide is white at ordinary temperatures, but clear yellow at 200°. It decomposes at 400° into the dioxide and metal. It reacts violently with water to form the hydroxide.

165 *Potassium Hydroxide, or Caustic Potash*, KOH.—This compound, generally known by its old name of caustic potash, was considered to be an oxide of potassium, but Darcet,[4] in the beginning of 1808, showed that ignited caustic alkali contains some other ingredient in addition to oxygen and the metal. He believed that this ingredient was in all probability water inasmuch as the calculated quantity of alkali contained in the carbonate neutralised more acid than the same quantity of the ignited caustic alkali. From this time forward caustic potash was considered to be a compound of potassium oxide and water, and it was not until a much later period that it was recognised to be a *hydroxide*, or a compound which is derived from water by the replacement of a portion of the hydrogen by a metal.

In order to obtain caustic potash, the metal may be allowed to act on water, but it is generally prepared by decomposing a dilute solution of potassium carbonate with slaked lime. For this purpose one part by weight of potassium carbonate is dissolved in twelve parts of water, the solution placed in an iron or silver vessel provided with a lid, heated to the boiling point, and then milk of lime gradually added until a portion of the filtered liquid evolves no carbon dioxide when treated with an acid. The solution is allowed to settle, and the clear liquid drawn off into a well-stoppered vessel. This is then evaporated in a silver basin until the hydroxide begins to volatilise. In order to ensure the complete separation of the carbonic acid from the potash, not less water than that mentioned must be used, and the water which evaporates from time to time must be renewed, for when only four parts of water are present to one part of potassium carbonate no decomposition takes place. A concentrated solution of caustic potash is found to decompose carbonate of calcium (Liebig).[5] A certain amount of the caustic potash of commerce is prepared in this way. It is usually cast in the

[1] Kühnemann, *Chem. Centr.*, 1863, 491. [2] *Journ. Chem. Soc.*, 1894, **65**, 438.
[3] *Compt. rend.*, 1907, **144**, 753. [4] *Ann. Chim.*, 1808, **68**, 175.
[5] See also Bodländer and Lucas, *Zeit. angew. Chem.*, 1905, **18**, 1137.

form of sticks which contain more or less water as well as all the impurities of the original potassium carbonate, especially alumina, potassium chloride, potassium sulphate, and potassium silicate. It may be purified by dissolving in alcohol in the manner already described for caustic soda (p. 245).

A large amount of caustic potash is now made in Germany by the electrolysis of solutions of potassium chloride, the process being similar to that employed for the production of caustic soda from salt (p. 311).

Pure caustic potash may also be obtained by adding powdered potassium sulphate to a hot concentrated solution of barium hydroxide (baryta water) until a small quantity of sulphate of potassium remains in excess; this is then removed by a careful addition of baryta water. The clear solution poured off from the insoluble barium sulphate is finally evaporated in a silver basin, any baryta which remains in solution being deposited in the form of carbonate by combination with the carbonic acid of the air.[1]

Attempts have been made to manufacture potash from the sulphate by the action of lime, but hitherto without success.[2]

Wöhler's process for obtaining pure caustic potash consists in decomposing pure potassium nitrate by metallic copper at a red heat.[3]

Properties.—Pure caustic potash is a hard, white, brittle substance, often exhibiting a fibrous structure, melting below a red heat to a clear oily liquid, and volatilising in the form of white vapours when more strongly ignited. The vapour of this substance decomposes, at a white heat, into potassium, hydrogen, and oxygen, and this decomposition explains, according to Deville, the formation of potassium by Gay-Lussac's method.

Caustic potash rapidly absorbs carbonic acid and moisture from the air, and dissolves in water with evolution of heat. According to Ferchland,[4] one part of water dissolves 1·07 parts of caustic potash at 15°. When the concentrated aqueous solution is cooled, the hydrate $KOH,2H_2O$ crystallises in transparent colourless acute rhombohedra which melt at 35·5°. Crystalline hydrates, $2KOH,9H_2O$ and $2KOH,5H_2O$ have also been described,[5] and Pickering[6] has obtained evidence of the existence

[1] Schubert, *J. pr. Chem.*, 1842, **26**, 117.
[2] Harold, *Zeit. Elektrochem.*, 1905, **11**, 417.
[3] *Annalen*, 1853, **87**, 373.
[4] *Zeit. anorg. Chem.*, 1902, **30**, 130
[5] Gottig, *Ber.*, 1887, **20**, 1094.
[6] *Journ. Chem. Soc.*, 1893, **63**, 898.

of KOH,H_2O, melting at 142°, and of $KOH,4H_2O$, melting at −32·7°. According to a German Patent, when solutions containing over 85 per cent. of hydroxide are cooled, anhydrous KOH crystallises out.[1]

The aqueous solution of caustic potash, sometimes known as *potash lye*, possesses an acrid taste and a peculiar nauseous odour; it acts as a powerful cautery, quickly destroying both animal and vegetable substances. For this reason its solution cannot be filtered except through glass or sand, and it is best clarified by subsidence. The following table gives the specific gravity at 15°/4° of solutions of potash of varying strength according to the experiments of Pickering:[2]

Per cent. of KOH.	Specific gravity.	Per cent. of KOH.	Specific gravity.
1	1·0083	30	1·2905
5	1·0452	35	1·3440
10	1·0918	40	1·3991
15	1·1396	45	1·4558
20	1·1884	50	1·5143.
25	1·2387		

The solution saturated at 15° has the sp. gr. 1·5355 and the concentration of 51·7 per cent. Caustic potash also readily dissolves in alcohol.

The *liquor potassæ* of the Pharmacopœia contains about 5 per cent. of the hydroxide KOH, and has a specific gravity of 1·058. Caustic potash is largely used in the form of a lye for absorbing carbon dioxide in both organic and inorganic analysis. It absorbs moisture very rapidly from the air, and may, therefore, be employed for drying certain gases and liquids, especially organic substances which do not dissolve it and are not acted upon by it. The chief commercial use, however, of caustic potash is for the manufacture of soft soap. The soap-maker formerly prepared his lye by lixiviation of wood-ashes, the solution thus obtained being causticised by boiling with milk of lime. At the present day the commercial carbonate is employed for this purpose, or caustic potash is bought ready for use.

Potassium Peroxide, K_2O_4.—This oxide was discovered by Gay-Lussac and Thénard. It is best obtained by heating potassium in excess of slightly moist air or oxygen. The metal takes fire at a temperature of from 60° to 80°, and when the

[1] D. R. P., 180835 (1906).

[2] *Phil. Mag.*, 1891 (5), **32**, 359.

surface is kept clean, burns to peroxide. In order to obtain the oxide in the pure state, clean potassium must be moderately heated, first in a current of dry air and then in dry oxygen. If the metal is at once exposed to oxygen, great heat is evolved and the glass is attacked. According to Vernon Harcourt,[1] it is best to bring clean dry potassium into a flask containing dry nitrogen, in which it is melted. The nitrogen gas is then gradually displaced by air; the grey film which covers the molten metal is seen to change to a deep blue; then a point is reached at which the rapid absorption of oxygen begins. Gradually, as the oxidation proceeds, the metallic coating of the inner surface of the bulb changes to a dead white; this, however, after a while assumes a yellow colour, due to the formation of the tetroxide. By the action of ozone on dry caustic potash an orange-yellow substance is formed, which is possibly identical with potassium peroxide.[2]

Potassium tetroxide is a dark chrome-yellow coloured powder, which fuses at a higher temperature than caustic potash, forming a black liquid, which, when the temperature falls, solidifies in lustrous tabular crystals; at a white heat, or when kept at a red heat for some time, it is decomposed into potassium monoxide and oxygen. When exposed to moist air it loses oxygen, forming possibly potassium dioxide:[3]

$$K_2O_4 = K_2O_2 + O_2.$$

Thrown on to water it dissolves with considerable evolution of heat, forming caustic potash, hydrogen peroxide, and free oxygen. Carbon monoxide acts upon the peroxide at a temperature somewhat below 100° with the formation of potassium carbonate, a volume of oxygen equal to that of the carbon monoxide employed being liberated thus:

$$K_2O_4 + CO = K_2CO_3 + O_2.$$

The heated oxide is also decomposed by carbon dioxide with liberation of oxygen, and by hydrogen.[4]

Phosphorus and sulphur act violently upon the peroxide with formation of potassium phosphate and sulphate. When metals such as potassium, arsenic, antimony, and zinc are heated with this compound, they are oxidised with evolution of light and

[1] *Journ. Chem. Soc.*, 1862, **14**, 267.
[2] Baeyer and Villiger, *Ber.*, 1902, **35**, 3038.
[3] Holt and Sims, *Journ. Chem. Soc.*, 1894, **65**, 437. [4] *Ber.*, 1897, **30**, 2515.

heat, whilst several metals such as bismuth, lead, iron, and silver undergo oxidation without the phenomenon of incandescence.

Potassium and Hydrogen.

166 *Potassium Hydride*, KH.—Potassium, when heated to 360° in hydrogen, yields the hydride KH, which crystallises in slender, white needles, and closely resembles the sodium compound (p. 249) in its properties.[1] It ignites spontaneously in fluorine, chlorine, or oxygen. When treated with moist carbon dioxide at the ordinary temperature, it is converted into potassium formate:[2]

$$KH + CO_2 = KHCO_2.$$

The absorption of hydrogen by potassium was previously observed by Gay-Lussac and Thénard, and by Troost and Hautefeuille,[3] who, however, did not obtain the crystalline hydride.

Potassium and the Halogens.

167 *Potassium Fluoride*, KF.—This is formed when aqueous hydrofluoric acid is neutralised in a platinum vessel with caustic potash or potassium carbonate, and the solution evaporated down. This salt crystallises from solutions above 40° in anhydrous cubes, below that temperature in prisms of the hydrate, $KF,2H_2O$. The saturated solution of this hydrate at 18° contains 48 per cent. of the anhydrous salt.[4] It is very deliquescent, has a sharp saline taste, and melts at 885°.[5] When it is dissolved in aqueous hydrofluoric acid it forms an acid fluoride, KF,HF, crystallising in tetragonal tablets. These melt when heated, and at a dark red heat decompose into potassium fluoride and hydrofluoric acid, this decomposition being employed for the preparation of anhydrous hydrofluoric acid. Crystalline compounds, KF,2HF and KF,3HF, have also been obtained by Moissan.[6] Potassium fluoride forms a large number of double salts.

Potassium Chloride, KCl, is a substance closely resembling rock-salt. Indeed in earlier times no distinction was drawn

[1] Moissan, *Compt. rend.*, 1902, **134**, 18.
[2] *Ibid.*, 1902, **134**, 261.
[3] *Ann. Chim. Phys.*, 1874 (5), **2**, 273.
[4] Mylius and Funk, *Ber.*, 1897, **30**, 1716.
[5] Ruff and Plato, *Ber.*, 1903, **36**, 2357.
[6] *Compt. rend.*, 1888, **106**, 547.

between these two compounds, but it was later known as *sal digestivum Sylvii* or *digestive salt.* It occurs in sea-water as well as in that of many mineral springs, and forms the chief portion of the Stassfurt potash-salt. This salt exists in a bed 20 to 30 metres in thickness, lying above the deposit of rock-salt, and consisting chiefly of polyhalite, $2CaSO_4,MgSO_4,K_2SO_4,2H_2O$; carnallite, $KCl,MgCl_2,6H_2O$; and kieserite, $MgSO_4,H_2O$, interspersed with layers or veins of tachydrite, $CaCl_2,2MgCl_2,12H_2O$; boracite, $2Mg_3B_8O_{15},MgCl_2$; kainite, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, and sylvine, KCl. These last two appear to be formed by the action of water upon the preceding compounds. In these minerals a small quantity of the potassium chloride is replaced by potassium bromide, and crystals of anhydrite $CaSO_4$, are found in the kieserite beds. The minerals composing this bed are all of them very deliquescent, and their position leads to the inference that the saline deposits at Stassfurt have been formed by the gradual evaporation of an inland sea or salt-water lake. This is rendered more probable by the fact that in the manufacture of sea-salt in the so-called salterns on the Mediterranean coasts similar salts are deposited from the mother-liquors. A very elaborate investigation into the conditions of formation of these minerals has been made by van't Hoff.[1] In addition to the deposits at Stassfurt, similar beds have been found at Kulusz, in the East Carpathians. These potash salts do not occur in the majority of saliferous beds, and this is probably due to the fact that the upper saline strata have in most cases been washed away, whereas in the Stassfurt deposit they have been protected by a water-tight stratum of clay.[2] The mode of manufacture of potassium chloride from these potash salts is almost identical with that proposed by Balard[3] and Merle[4] for the preparation of the chloride from sea-water, and by Hermann[5] for preparing it from certain mineral springs.

The method depends on the fact that carnallite is easily soluble in a hot solution of magnesium chloride, whereas sodium chloride and magnesium sulphate are only slightly soluble in this liquid, and that when the hot liquor is allowed to cool the double salt does not separate out, but the more soluble mag-

[1] Zur Bildung der ozeanischen Salzablagerungen (Braunschweig, 1905).

[2] For a full account of these deposits, see Thorpe's *Dict. of Appl. Chem.*, vol. iii. 265.

[3] *Jahresb. Chem. Technol.*, 1865, 296.

[4] *Bull. Soc. Chim.*, 1868, [2], **10**, 63. [5] *J. pr. Chem.*, 1853, **60**, 284.

nesium chloride remains in solution whilst a part of the chloride of potassium crystallises out. The crude carnallite is crushed and treated with a mixture of the mother-liquors resulting from later processes of the manufacture, and steam is passed in. After separation of the suspended insoluble matter and the sodium chloride and kieserite, the liquor is run into crystallising vessels and allowed to cool gradually, a large proportion of crude potassium chloride separating out. The mother-liquor is then concentrated, and on cooling yields a further deposit of the crude chloride. The crude potassium chloride is purified by washing first with washing liquor from a former operation, and finally with water, the impurities removed being sodium chloride and magnesium chloride and sulphate. The quantity of potassium chloride in the various commercial products is from 75 to 98 per cent.[1]

In the salines on the west and south coasts of France the mother-liquors remaining after the common salt has been deposited, having a specific gravity of 1·22, are preserved in reservoirs during the summer, when a mixture of magnesium sulphate and common salt (*sel mixte*) separates out. The mother-liquor from this is evaporated in flat pans and thus converted into carnallite, which is worked up as described.

Potassium chloride crystallises like sodium chloride, in cubes. It has a cooling saline taste and a specific gravity of 1·995: it melts at 790° (Ruff and Plato), and readily volatilises at a bright red heat. 100 parts of water dissolve 28 parts of potassium chloride at 0°, 32·7 parts at 15°, and 56·5 parts at 100°.

When potassium chloride is melted in a current of hydrogen gas, or when the fused salt is subjected to electrolysis, a dark blue mass is formed which probably contains a sub-chloride of potassium, the composition of which has not been satisfactorily ascertained.

Potassium chloride is used for the preparation of other potassium compounds such as the chlorate, the carbonate, the chromate, the hydroxide, the nitrate and potash alum, but by far the greatest quantity is used for the preparation of artificial manures, for which purpose the crude salt is employed.

Potassium Bromide, KBr.—When bromine is dissolved in caustic potash a mixture of bromide and bromate of potassium is formed. If this mixture be evaporated and gently ignited, the bromate is decomposed, and pure potassium bromide is left.

[1] See *Ber. über Entwickl. Chem. Industrie*, 1, 351.

The usual method of preparing the salt on the large scale is by the action of bromine and water on iron filings; the bromide of iron thus formed being then decomposed by potassium carbonate.

Potassium bromide crystallises in cubes possessing a sharp saline taste, melts at 750°, and volatilises at a high temperature; 100 parts of water at 15° dissolve 62 parts of the salt. It serves as a valuable medicine, especially in cases of nervous diseases. It unites with bromine,[1] forming a very unstable tribromide, KBr_3.

Potassium Iodide, KI.—This salt is prepared in a similar way to the bromide. It crystallises, like the two former salts, in cubes, which possess a sharp taste. Potassium iodide melts at 685° (Meyer, Riddle, and Lamb), 705° (Ruff and Plato), and can be easily vaporised at a higher temperature, the vapour having a normal density. 100 parts of water dissolve at 0°, 127·9, and at 118·4°, the boiling point of the saturated solution, 222·6 parts of the salt, whilst at intermediate temperatures the solubility increases proportionally to the rise of temperature (Mulder). Potassium iodide is sparingly soluble in absolute alcohol, and is soluble also in acetone and glycerol. The commercial iodide of potassium generally possesses an alkaline reaction; in order to obtain it perfectly neutral it must be dissolved in the smallest quantity of water, neutralised with dilute sulphuric acid, the potassium sulphate precipitated by the addition of pure alcohol, and the solution allowed to crystallise (Groves). Potassium iodide is largely used in medicine both for internal and for external application, especially in scrofulous and syphilitic diseases.

Potassium Tri-iodide, KI_3.—This compound is formed by saturating a concentrated solution of potassium iodide with iodine. A brown liquid having a metallic lustre is obtained, and this on evaporation over sulphuric acid yields needle-shaped almost black crystals which possess a metallic lustre. They are very deliquescent and readily lose iodine when gently heated (Johnson).[2]

Experiments on the distribution of iodine between carbon disulphide and potassium iodide solution show that this salt is dissociated in solution into the ions $K^{\cdot}$ and I_3', and is to be regarded as the salt of an acid, HI_3, which belongs to the class

[1] See Worley, *Journ. Chem. Soc.*, 1905, **87**, 1107; Jakowkin, *Zeit. physikal. Chem.*, 1896, **20**, 719.

[2] *Journ. Chem. Soc.*, 1877, 249.

of strong acids.[1] There is, moreover, some evidence that the compound KI_9 exists in solution in nitrobenzene and other similar solvents.[2]

According to Abegg, the only solid polyiodide of potassium which can exist at 25° is KI_7, but this salt has not been actually isolated.[3]

Potassium Iodotetrachloride, $KICl_4$, was prepared by Filhol in 1839, by the action of chlorine on a solution of potassium chloride containing iodine. It forms lustrous, golden yellow crystals.

168 *Potassium Hypochlorite*, KClO.—When chlorine is passed into a dilute cold solution of caustic potash or potassium carbonate, a mixture of potassium chloride and potassium hypochlorite is obtained. This liquid was first prepared by Berthollet, and the solution, known by the name "Eau de Javelle," was formerly largely used for bleaching purposes (see Vol. I., p. 345). It can also be prepared by electrolysis of potassium chloride solutions. Pure potassium hypochlorite has not yet been prepared.

Potassium Chlorate, $KClO_3$.—It appears likely that this salt was known to Glauber. In one of his works he mentions that he is acquainted with a means of converting muriatic acid into nitric acid, and in his "Continuatio Miraculi Mundi" he mentions a peculiar kind of saltpetre which he had prepared by means of common salt. This was probably potassium chlorate. In like manner Winterl, in 1789, believed that he had converted muriatic acid into nitric acid by strongly heating muriate of lime (calcium chloride) in a retort with black oxide of manganese and leading the product into a receiver containing a small quantity of caustic potash. Higgins also stated in 1786 that by the action of dephlogisticated muriatic acid (chlorine) on the alkalis, a peculiar kind of saltpetre is formed. Potassium chlorate was afterwards prepared by Berthollet in his classical investigation of the action of chlorine on the alkalis in 1786.

Manufacture.—This salt was formerly produced on the large scale by passing chlorine into a concentrated solution of caustic potash or potassium carbonate; being only slightly soluble in water it crystallises out when the solution is cooled. The

[1] Jakowkin, *Zeit. physikal. Chem.*, 1896, **20**, 19; Dawson, *Journ. Chem. Soc.*, 1901, **79**, 238.

[2] Dawson and Gawler, *Journ. Chem. Soc.*, 1902, **81**, 524; Dawson, *ibid.*, 1904, **85**, 467.

[3] *Zeit. anorg. Chem.*, 1906, **50**, 414.

product of these and any similar reactions is a hypochlorite so long as the alkali remains in excess:

$$2KOH + Cl_2 = KOCl + KCl + H_2O,$$

but directly the alkali is exhausted and the chlorine is present in excess the hypochlorite is suddenly converted with evolution of a considerable amount of heat into chlorate:

$$3KOCl = KClO_3 + 2KCl.$$

In order to use a less expensive potassium salt and also less of it, chlorine is passed into milk of lime until the chlorate is formed:

$$6Ca(OH)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O;$$

the clear settled liquor is concentrated by evaporation and a quantity of potassium chloride exactly equivalent to the calcium chlorate present is added; on cooling potassium chlorate crystallises out. From 1870 this process has been carried out on a very large scale in Widnes and St. Helens, the output for 1887 being 5,500 tons. Large quantities, however, are now made electrolytically elsewhere A very complete description of this industry has been given by Jurisch.[1]

The lime process is now being largely supplemented by a modification of Berthollet's original caustic potash method, in which the caustic potash and the chlorine are simultaneously formed by the electrolysis of a solution of potassium chloride and immediately react upon each other; by repeating the operation upon the mother-liquors after cooling, the original solution is ultimately converted into potassium chlorate and hydrogen:

$$KCl + 3H_2O = KClO_3 + 3H_2.$$

The process was introduced in 1886 by Gall and Montlaur in Switzerland, and is now also in use in France, Germany, Austria, Sweden, and the United States, the necessary current being obtained in each case from water power. A description of the process has been published by Kershaw.[2] The yearly output of potassium chlorate is probably over 20,000 tons, the main portion of which is prepared electrolytically.

Properties.—Potassium chlorate crystallises in large transparent monoclinic tablets having a glassy lustre; these

[1] *Die Fabrikation von chlorsaurem Kali*, 1888.

[2] *Die elektrolytische Chloratindustrie*, 1905.

when they are of certain dimensions, exhibit magnificent iridescent colours, and emit light when rubbed in the dark. The crystals of potassium chlorate have a feebly acid and cooling taste similar to that of nitre. They have the sp. gr. 2·35, melt without decomposition at 359° (Carnelley), and at 372° they begin to decompose with evolution of oxygen. The nature of the decomposition and the effect of the addition of certain oxides has already been discussed (Vol. I., p. 241). 100 parts of water dissolve at 0°, 3·3 parts, at 20°, 7·1 parts, and at 104·2°, the boiling point of the saturated solution, 61·5 parts of the salt (Gay-Lussac, Legrand).

Potassium chlorate is largely used in the laboratory for the preparation of oxygen gas. It also acts as a powerful oxidising agent and is employed in the manufacture of lucifer matches and certain explosives, for pyrotechnic purposes, and in calico printing. In large doses it acts as an irritant poison, like nitre and other soluble potassium salts. It was formerly given in small doses in cases of scarlet fever, scurvy, and other diseases, as it was believed to act as an oxidising agent on the blood, but it has been shown that the whole of the salt passes out undecomposed in the urine. It is still employed as a gargle for the purpose of allaying inflammation of the throat.

The powerful oxidising properties of potassium chlorate can be readily exhibited. If a small quantity of the powdered salt be thrown on to glowing charcoal, a rapid combustion takes place. If a few grains of this salt, together with a few grains of flowers of sulphur, are rubbed together in a mortar, loud explosions occur, and if a grain of the mixture be struck with a hammer a loud detonation takes place. Only very small quantities of the mixture must be used, as otherwise the explosions may become dangerous. Further, if a small quantity of red phosphorus be carefully mixed by means of a feather with the same quantity of powdered potassium chlorate, the mixture will explode when struck even a slight blow with a glass rod. This may also be shown by allowing a few drops of a solution of phosphorus in carbon disulphide to fall on powdered potassium chlorate; after a few moments a violent explosion occurs.

Potassium Perchlorate, $KClO_4$.—The preparation of this salt by heating potassium chlorate has already been described and explained in Vol. I., p. 357. It is also prepared by the electrolytic oxidation of potassium chlorate in neutral or acid

solution,[1] or more conveniently by submitting sodium chlorate to this treatment and then adding potassium chloride. It forms small rhombic crystals which possess a slightly saline taste and melt at about 610°; 100 parts of water dissolve at 0°, 0·71 part, at 50°, 5·34 parts, and at 100°, 18·7 parts of salt (Muir); it is almost insoluble in strong alcohol, and is therefore used for the quantitative estimation of potassium.

Potassium Bromate, $KBrO_3$, is obtained according to Stas, by passing chlorine into a warm solution of potassium bromide and caustic potash:

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O.$$

A portion of the salt crystallises out on cooling, and the remainder is precipitated on addition of alcohol, together with a little potassium chloride, from which it is easily separated by recrystallisation. According to Marignac, it forms hexagonal (ditrigonal pyramidal) crystals and separates out in six-sided tablets or prisms which have the appearance of cubes. 100 parts of water dissolve 6·9 parts of the salt at 20°, and 49·8 parts at 100°. It melts at 434°, and is converted by ignition into potassium bromide and oxygen, bromine being also evolved when it is heated slowly.

Potassium Iodate, KIO_3, is formed together with the iodide by the action of iodine on caustic potash, but it is most readily obtained by heating potassium chlorate with iodine:

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2;$$

the liberated chlorine combines with excess of iodine to form iodine mono- and tri-chloride.[2] Potassium iodate crystallises in small cubical crystals, melts at 560°, and begins to decompose at a much higher temperature than the chlorate. 100 parts of water dissolve 8·1 parts of the salt at 20°, and 32·3 parts at 100°. It combines with iodic acid to form the compounds KIO_3,HIO_3, and $KIO_3,2HIO_3$ (see Vol. I., p. 369).

Potassium Periodate, KIO_4, is formed when chlorine is passed through a mixture of caustic potash and potassium iodate. It can also be obtained electrolytically by the anodic oxidation of potassium iodate. It separates out as shining crystals which are isomorphous with those of potassium perchlorate, and melt

[1] Foerster, *Zeit. Elektrochem.*, 1898, **4**, 386.

[2] Thorpe and Perry, *Journ. Chem. Soc.*, 1892, **61**, 925. See also Schlötter, *Zeit. anorg. Chem.*, 1905, **45**, 270.

at 582°. When a hot concentrated solution of the salt is mixed with alcoholic potash, rhombohedra of *potassium meso-periodate*, $K_3IO_5,4H_2O$, are deposited. These have an alkaline reaction, and absorb carbon dioxide from the air. When the normal salt is evaporated together with caustic potash, triclinic prisms of *potassium di-periodate*, $K_4I_2O_9,9H_2O$, are deposited, which have an alkaline reaction (see also Vol. I., p. 363).

POTASSIUM AND SULPHUR.

169 *Potassium Monosulphide*, K_2S.—This substance is formed, according to Berzelius, by passing hydrogen over heated potassium sulphate. It forms a pale red crystalline mass, which becomes darker on heating, and melts to a black liquid below a red heat. Berthier obtained the same compound as a flesh-coloured mass by strongly heating the sulphate with carbon:

$$K_2SO_4+4C=K_2S+4CO.$$

In order, however, to obtain this substance a larger amount of carbon is needed than that represented in the above equation; otherwise a mixture of higher sulphides with potassium carbonate is obtained (Wittstock). Indeed it appears impossible to obtain perfectly pure monosulphide in this way, as even the substance obtained by reduction with hydrogen contains higher sulphur compounds.[1] The mass deliquesces in moist air, and dissolves in water with a considerable evolution of heat.

If potash lye be saturated with sulphuretted hydrogen, and if then an equal quantity of alkali be added to the liquid, a solution of the monosulphide is obtained. This remains colourless if the air be excluded, possesses an alkaline taste, and acts on the skin as a strong caustic. When evaporated in a vacuum at a low temperature, four-sided prisms are deposited, having the formula $K_2S,5H_2O$.[2] Hydrates with $12H_2O$ and with $2H_2O$ have also been obtained (Bloxam). If this aqueous solution is boiled, only traces of sulphuretted hydrogen are given off, and when exposed to the air it becomes yellow from absorption of oxygen and carbon dioxide, and formation of potassium thiosulphate and potassium carbonate; the sulphuretted hydrogen which is

[1] Bauer, *J. pr. Chem.*, 1858, **75**, 246.
[2] Schöne, *Pogg. Ann.*, 1867, **131**, 380.

liberated decomposes with formation of water and sulphur, and the latter substance unites with the monosulphide to form higher sulphides. On shaking the yellow solution with metallic copper it again becomes colourless. The main product of the action of air free from carbon dioxide on a solution of the monosulphide is sulphite, the liquid remaining colourless.

Potassium Hydrosulphide, KSH.—This substance was first prepared by Gay-Lussac by heating potassium in dry sulphuretted hydrogen. He then observed that the same quantity of potassium which was capable of evolving one volume of hydrogen from water was able to combine with all the sulphur in two volumes of sulphuretted hydrogen, liberating half the hydrogen:

$$2K + 2H_2S = H_2 + 2KSH.$$

Berzelius obtained the same compound by the action of sulphuretted hydrogen on carbonate of potassium heated to dull redness, but the product of this reaction is by no means pure (Bloxam):

$$K_2CO_3 + 2H_2S = 2KSH + H_2O + CO_2.$$

It can be obtained pure by passing sulphuretted hydrogen through anhydrous ether in which metallic potassium is placed.[1] This body forms a white or yellowish deliquescent mass, which when heated to 450°−510° melts to a liquid, and at a higher temperature becomes of a dark red colour. It is very soluble in water, and the aqueous solution is very easily obtained by saturating caustic potash solution with sulphuretted hydrogen. This forms a colourless liquid which smells slightly of sulphuretted hydrogen, has an alkaline and bitter taste, decomposes very slowly when boiled, and on exposure to air containing carbon dioxide becomes yellow owing to the formation of higher sulphides. When exposed for a still longer time to the action of the air it becomes colourless, inasmuch as potassium thiosulphate is formed. If the concentrated solution is allowed to evaporate over caustic lime or caustic soda in a vacuum, colourless glittering rhombohedral crystals separate out, having the formula $2KSH,H_2O$.

A number of polysulphides have been described, having the formulæ K_2S_2, K_2S_3, K_2S_4, and K_2S_5, which are obtained by the action of sulphur, sulphuretted hydrogen, or carbon disulphide

[1] Bloxam, *Journ. Chem. Soc.*, 1900, **77**, 758.

vapour on the monosulphide, or compounds which readily yield it. They are described as yellowish-red or dark red substances, which dissolve readily in water. Spring and Demarteau,[1] however, regard these polysulphides as solid solutions of sulphur in the monosulphide, as in their reactions with iodine, potassium sulphite, and ethyl iodide, they behave as mixtures of these two substances. They are also all reduced to the monosulphide when their solutions are shaken with mercury.

Crystalline polysulphides of the formulæ K_4S_8, K_4S_9, and K_4S_{10} have also been obtained by the action of potassium hydrosulphide on sulphur. The first two when treated with carbon disulphide yield the stable yellow sulphide K_4S_5.[2] They all take up water of crystallisation.

Liver of Sulphur or Hepar Sulphuris.—This is an old name given to a mixture of potassium polysulphides with potassium sulphate, or potassium thiosulphate. It is obtained by gently heating sulphur with carbonate of potassium in a covered vessel. The composition of the liver-coloured mass thus obtained is variable, according to the proportions in which the bodies have been mixed and the temperature to which they have been heated. Liver of sulphur was well known to the alchemists of the middle ages. Stahl considered it to be a compound of the alkali with sulphur, and called it "sulphurised alkali." He also knew that it could be prepared by heating sulphate of potash with carbon, and used this fact to prove that only one kind of phlogiston exists (see Vol. I., p. 14). Liver of sulphur is used in medicine, and is termed in the Pharmacopœia, *potassa sulphurata.* It is used also by gardeners to get rid of mildew and exterminate insect pests.

170 *Potassium Sulphite,* K_2SO_3, is prepared by dissolving 100 grams of caustic potash in 200 c.c. of water previously freed from dissolved air, and saturating with sulphur dioxide; a further quantity of 100 grams of caustic potash dissolved in a very small volume of water is then added, and the solution allowed to evaporate in vacuo. Potassium sulphite separates in small deliquescent hexagonal crystals which are more soluble in cold than in hot water. The *monohydrated salt,* K_2SO_3,H_2O, is obtained by dissolving the metabisulphite in water, adding an equivalent quantity of caustic potash, evaporating and allowing

[1] *Bull. Soc. Chim.*, 1899 (3), **1**, 311.
[2] Bloxam, *Journ. Chem. Soc.*, 1900, **77**, 767.

to crystallise. The *dihydrated salt*, $K_2SO_3,2H_2O$, is obtained when the solution is allowed to evaporate over sulphuric acid, and forms oblique rhombic octahedra, which possess a bitter alkaline taste, and are also more soluble in cold than in hot water. The solutions readily undergo oxidation in the air.

Two isomeric potassium sodium sulphites, $Na.SO_2.OK$ and $K.SO_2.ONa$, are also known. These have already been described in Vol. I., p. 398.

Potassium Hydrogen Sulphite, $KHSO_3$, is produced when a solution of the normal salt or of caustic potash is saturated with sulphur dioxide. On addition of alcohol it separates out in needle-shaped crystals, which taste of sulphurous acid, and have a neutral reaction.

Potassium Metabisulphite, $K_2S_2O_5$, is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate (Muspratt), or into a mixture of milk of lime and potassium sulphate (Boake and Roberts). It forms monoclinic crystals which are sparingly soluble in water and have an unpleasant acid taste. Potassium metabisulphite is employed in photography.

171 *Potassium Sulphate*, K_2SO_4.—The mode of preparing this salt was known as early as the fourteenth century. It was first obtained from the residues of the manufacture of *aqua fortis*, and afterwards by the action of sulphuric acid on crude potashes. Potassium sulphate is probably one of the salts whose constituents were first determined by analysis. Glauber, Boyle, and Tachenius were acquainted with its composition, and in the seventeenth century it was termed *arcanum* or *sal duplicatum*, because, according to the then prevalent ideas, it was made up of an acid salt and an alkaline salt. The decomposition of this salt into its constituent parts was at that time supposed to be a most difficult matter. Indeed, Stahl proposed the following question to the French Academy : How is it possible to decompose this salt instantly when held in the hand? Although none of the Academicians were able to answer this question, Stahl accomplished his purpose by adding nitrate of silver, which at once separated vitriolic acid from the alkali.

Potassium sulphate is found native in the lavas of Vesuvius. It is also obtained from the kainite, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, and schönite, $K_2SO_4,MgSO_4,6H_2O$, of the Stassfurt beds and of those of Kulusz, and as a by-product in several chemical manufactures, such as that of potassium dichromate, as well as in the

lixiviation of kelp. It is now manufactured by the double decomposition of potassium chloride and magnesium sulphate in aqueous solution, and is also prepared to a small extent by the action of sulphuric acid on the chloride.[1]

Potassium sulphate crystallises in small, hard, rhombic pyramids, possessing a hexagonal or prismatic habit; it has a specific gravity of 2·6633 at 20°/4° (Tutton), and melts at 1050°. One hundred parts of water at 15° dissolve 10·3 parts of this salt, whilst 24·1 parts dissolve in the same quantity of water at 100°. Aqueous alcohol dissolves it in quantities proportional to the amount of water which the alcohol contains. The salt is quite insoluble in a solution of caustic potash of specific gravity 1·35 (Liebig), and in absolute alcohol. It has a bitter saline taste and can be volatilised only at a very high temperature.

Potassium sulphate is used as a purgative, and is employed in large quantities for the manufacture of potash alum and potassium carbonate. Potassium sulphate itself as well as the mineral kainite and the double salt $K_2SO_4,2MgSO_4,H_2O$, which is prepared from it, are also very largely used as fertilisers.

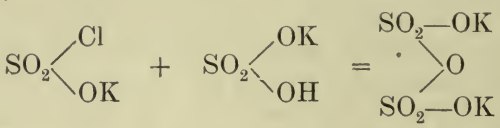
Potassium Hydrogen Sulphate, $KHSO_4$.—In 1754, Rouelle proved that in addition to the *arcanum duplicatum*, other salts exist containing an excess of acid chemically combined. Amongst these he mentions acid potassium sulphate, which he obtained in the crystalline state. The same salt is found native in the Grotto del Sofo, near Naples, in the form of long silky needles. It is frequently obtained in the laboratory as a by-product in the preparation of nitric acid from saltpetre and sulphuric acid. It crystallises in rhombic pyramids, according to Marignac, in rhombohedra according to Jacquelain, has a specific gravity of 2·163, melts at 197°, dissolves readily in water, and possesses an acid saline taste. When brought into contact with alcohol it is decomposed into sulphuric acid and the normal salt, which is insoluble in this liquid. When the acid sulphate is recrystallised from aqueous solution the normal salt is found to separate out first, then crystals of a salt having the composition $K_2SO_4,KHSO_4$ are deposited, and at last the acid sulphate crystallises out. Salts of the formulæ $K_2SO_4,3KHSO_4$ and $K_2SO_4,6KHSO_4$ have also been described.[2]

Potassium Disulphate, $K_2S_2O_7$.—This salt is obtained by

[1] Precht, *Zeit. angew. Chem.*, 1906, **19**, 1.

[2] Stortenbeker, *Rec. trav. chim.*, 1902, **21**, 399.

gently igniting the normal salt with sulphuric acid until the mass fuses quietly. It is also formed when the acid salt is heated with potassium chlorosulphonate, a compound obtained by the action of sulphur trioxide on potassium chloride:



The salt crystallises on cooling in long needles which decompose when brought into contact with water, evolving much heat and yielding the acid sulphate. When dissolved in fuming sulphuric acid this salt deposits transparent prismatic crystals of potassium hydrogen disulphate, KHS_2O_7.

Potassium thiosulphate, $K_2S_2O_3$, is prepared in a similar manner to, and closely resembles the corresponding sodium salt. Two isomeric sodium potassium thiosulphates are also known (Vol. I., p. 448).

Potassium Persulphate, $K_2S_2O_8$.—This salt is obtained by the electrolysis of a saturated solution of potassium hydrogen sulphate, and forms large tabular crystals which are sparingly soluble in water. Details of its preparation and properties have already been given in Vol. I., p. 445.

Potassium Selenate, K_2SeO_4, is isomorphous with potassium sulphate. It has the sp. gr. 3·0657 at 20°/4°, deliquesces in the air, and dissolves to the extent of 115 parts in 100 parts of water at 12°.[1] When a solution of this salt and selenic acid is electrolysed, a *perselenate* is formed,[2] which probably has the formula $K_2Se_2O_8$.

Potassium Azoimide, N_3K, can be prepared by neutralising hydrazoic acid with potassium hydroxide, or by the action of nitrous oxide on potassamide,

$$2KNH_2 + N_2O = N_3K + NH_3 + NaOH.$$

Potassium and Nitrogen.

172 *Potassamide*, NH_2K.—This compound was discovered by Gay-Lussac and Thénard in 1811. It is prepared by gently heating potassium in ammonia gas, and is usually obtained as an

[1] Tutton, *Journ. Chem. Soc.*, 1897, **71**, 846.

[2] Dennis and Brown, *J. Amer. Chem. Soc.*, 1901, **23**, 358.

olive-green or brown mass, but when the potassium is heated in a silver boat, it forms a white waxy crystalline mass, which melts at 272—274° and sublimes above 400°.[1] It quickly decomposes in moist air, yielding caustic potash and ammonia, and when water is added the same decomposition takes place with rapid liberation of heat, and frequently also of light. When strongly heated, it slowly undergoes decomposition into its elements, but does not, according to Titherley, leave a residue of the black potassium nitride described by Davy, which probably does not exist.

Potassium Nitrite, KNO_2, is formed when saltpetre is heated until one-third of the oxygen is evolved (Mitscherlich). The residue invariably contains undecomposed nitrate, and also oxides of potassium. The above decomposition takes place more readily in the presence of metallic iron, copper, or lead (Stromeyer). In order to prepare it in this way two parts of lead may be employed to one part of saltpetre. The latter salt is fused, and the fused mass heated to dull redness, the lead then added little by little, and the cooled mass lixiviated with water. On evaporation, or on neutralising in the cold with dilute sulphuric acid and adding to the solution twice its weight of alcohol, crystals of the nitrite are precipitated.

Pure potassium nitrite is best prepared by decomposing silver nitrite with potassium chloride (Berzelius), by decomposing amyl nitrite with the exactly necessary quantity of alcoholic potash (Chapman), by passing nitrous fumes into caustic potash (Divers),[2] or by the electrolysis of a solution of potassium nitrate.[3] It forms small indistinct, yellowish, anhydrous crystals which deliquesce in moist air, are soluble in one-third of their weight of water, and are insoluble in alcohol. This salt is employed for the separation of cobalt and nickel, and also in organic chemistry.

173 *Potassium Nitrate, Saltpetre, or Nitre*, KNO_3.—This remarkable salt was known to the ancients, being termed *Sal petræ* by the Latin Geber. It was frequently called *Sal nitri* by the later alchemists, to distinguish it from *nitrum*, by which name the ancients signified the native carbonate of soda, a salt which was not unfrequently mistaken for nitre. When trade between the East and the West increased, the mineral

[1] Titherley, *Journ. Chem. Soc.*, 1894, **65**, 511.
[2] *Journ. Chem. Soc.*, 1899, **75**, 86.
[3] Duparc, Couchet and Schlosser, *Zeit. Elektrochem.*, 1906, **12**, 665.

alkali was imported under the special name of natron, and then the word nitrum was specially reserved to designate saltpetre.

Saltpetre occurs, together with other nitrates, as an efflorescence on the soil in various hot countries, especially in Bengal, but likewise in Egypt, Syria, Persia, and Hungary, as well as in America. In Ceylon[1] and India nitre is obtained by the lixiviation of certain porous rocks, whence the origin of the word sal-petræ. These yield from 2·5 to 8 per cent. of their weight of nitre. The formation of nitre, whether found in the soil or in porous felspathic rocks, is due to the gradual oxidation of nitrogenous organic matter in contact with an alkali in presence of a nitrifying organism. In the decay and putrefaction of such bodies ammonia is first formed and is then converted first into nitrous and finally into nitric acid. Nitre is also found in the juices of certain plants. This fact was first pointed out by L. Lemery in 1717. Certain species of amaranthus, especially *A. atropurpureus*, contain no less than 22·7 per cent. of nitre in the dry plant (Boutin).

In India, a caste of men termed Sorawallahs,[2] from *sora*, nitre, at one time made it the business of their lives to collect the raw material, and to manufacture and sell the salt, which, before the introduction of cheap artificial ice, was employed locally for producing frigorific mixtures and was also largely exported.

"The *Sorawallah* goes about the village, examining the small surface drains which issue from holes in the mud-wall, usually found around native dwellings and their cow-houses; when he detects a faint white veil-like patch of crystalline formation, on or near the dark-coloured borders of these little drains, he knows that a considerable quantity of nitre exists, on or near the surface of all the surrounding earth; he accordingly proceeds to scrape off a very thin layer of the surface soil, which he carries away to his place of manufacture, as soon as his morning's collections are finished. On arriving there, the impregnated earth so collected is thrown into an earthen vessel containing either water or water which has been poured off from previous supplies of similarly impregnated earth." The liquid thus obtained was allowed to evaporate and the nitrate of potash recrystallised once or twice. "The *Sorawallah* makes fresh collections from precisely the same spots of ground from week to week, year to year, and from generation to generation

[1] John Davy, *Quart. Journ. Sci.*, 1818, **5**, 233.

[2] Palmer, *Journ. Chem. Soc.*, 1868, **21**, 318.

after the manner of the Eastern world; the production of nitre is constant so long as the place continues to be inhabited; it even continues to appear in large, though gradually decreasing, quantities, for years after the village may have been deserted. The intervals at which fresh collections may be made from the same spot vary in different localities and in different seasons of the year, from one to seven, ten, or more days."

This production of nitre is doubtless preceded by the formation of nitrate of calcium, and this, by double decomposition with potassium carbonate, yields nitre and calcium carbonate. Indian saltpetre was introduced into Europe by the Italians, and first employed for medicinal and chemical purposes.

When the demand for gunpowder became great, nitre began to be manufactured in Europe. Agricola, in his celebrated treatise *De Re Metallica*, describes the process of refining saltpetre as follows :—"Saltpetre is obtained from a dry somewhat fatty earth, which is boiled with quick-lime and wood-ashes. The mass is then lixiviated and the solution evaporated."[1] During the blockade of the French ports, the artificial production of nitre was of necessity largely carried on in that country. For this purpose nitrogenous organic matter of animal or vegetable origin, after having been allowed to putrefy by exposure to air in a dark place was mixed with substances such as lime, mortar, or wood-ashes, containing the carbonates of potash, magnesia, or lime. The mixture was then heaped together in ridges (saltpetre walls), or in low heaps (saltpetre mounds), which were then moistened from time to time by the drainage of dung heaps, or by urine, and exposed to the air. After standing for from two to three years the outer surface or saltpetre earth was removed and exhausted with water. This yielded the crude saltpetre ley which contained the nitrates of calcium and magnesium together with the chlorides of potassium and sodium. On boiling this liquor with potashes the calcium and magnesium salts were decomposed, and the clear solution was then crystallised. *Raw nitre* was thus obtained, and this by repeated solution and crystallisation was converted into *purified nitre*. In order still further to purify the salt, it was dissolved in boiling water, and the solution constantly agitated when cooling. The salt then separated out in small crystals termed *saltpetre-flour*, which enclosed much less of the mother liquor, and therefore much less impurity than the large crystals. This

[1] Berzelius, *Traité*, 3, 119.

finely-divided salt was then again purified by washing it with a saturated solution of pure nitre which dissolved out the last portions of foreign salts, thus rendering the saltpetre free from chlorides and fit to be employed in gunpowder-making.

Since the discovery of large quantities of potassium chloride at Stassfurt, this salt has been almost exclusively used for the artificial manufacture of saltpetre. This manufacture depends upon the fact that under certain conditions of temperature and pressure, solutions of Chili saltpetre (sodium nitrate), $NaNO_3$, and of potassium chloride undergo, when mixed, a double decomposition, chloride of sodium being deposited and potassium nitrate remaining in solution. For this purpose equivalent quantities of sodium nitrate and potassium chloride are dissolved in the mother-liquor from a previous operation and heated by steam for about half an hour. The product is run into strainers where it is kept hot, the greater part of the sodium chloride separating out under these conditions; the filtered liquor is then allowed to cool, and the resulting saltpetre meal, which contains 7 to 9 per cent. of sodium chloride and a little magnesium chloride, is purified by washing with mother-liquors resulting from subsequent washings, recrystallised, and finally washed with small quantities of pure water.

Saltpetre occurs in commerce in the form of small well-formed crystals, as well as in the form of flour. These are much purer than the larger crystals, which are often hollow and contain chloride of potassium and other impurities. About 10,000 tons per annum are imported into the United Kingdom.

Properties.—Potassium nitrate is dimorphous.[1] It usually crystallises in rhombic prisms, which not unfrequently closely resemble regular six-sided prisms. If, however, a few drops of a solution of nitre be allowed slowly to evaporate, rhombohedral crystals are deposited, isomorphous with those of sodium nitrate, but these are very unstable and when touched are converted into an aggregate of small rhombic crystals.

The rhombohedral form is stable above 129°, and a second rhombohedral form is known which is stable at a still higher temperature.[2]

Saltpetre has a specific gravity of 2·1; it melts at 339°

[1] Miller, *Phil. Mag.*, 1840 (3), **17**, 38.
[2] Wallerant, *Compt. rend.*, 1905, **140**, 264.

(Person), and possesses a bitter cooling saline taste. It dissolves in water with absorption of much heat. This property of nitre was first pointed out by the Spanish physician Blasius Villafranca, in his tract published in 1550, entitled "Methodus refrigerandi ex vocato Sale-nitro vinum aquamque ac potus quodvis aliud genus." According to Rüdorff, 16 parts of nitre when dissolved in 100 parts of water at 13·2° lower the temperature to +3°.

One hundred parts by weight of water dissolve :—

At	0°	10°	20°	40°	60°	80°	100°
KNO_3	13·3	20·9	31·6	63·9	109·9	169	246,

whilst at 114·1°, the boiling point of the saturated solution, 311 parts of the salt are dissolved.

Saltpetre is used in the laboratory, in medicine, for the salting or pickling of meat, to which it imparts a red colour, and for pyrotechnic purposes, but chiefly in the manufacture of gunpowder.

A salt of the composition $KNO_3,2HNO_3$, which is known as potassium trinitrate, crystallises out when a solution of potassium nitrate (1 mol.) in highly concentrated nitric acid (2 mols.) is cooled to −3°; the salt forms prisms which melt at 22°, and are decomposed by water. An unstable salt KNO_3,HNO_3 is also known, which crystallises in plates.[1]

Nitre used in Explosives.[2]—The Chinese are said to have been acquainted with the mode of manufacturing gunpowder from early times, although employing it rather for making fireworks than for warlike purposes. It appears probable that the knowledge of this manufacture resulted from an improvement in the preparation of Greek fire, which was discovered in 673 A.D., and itself consisted of combustible and fusible substances such as pitch, resin, and sulphur, mingled with crude saltpetre. In the *Liber ignium* of Marcus Graecus, a work which dates from the early part of the thirteenth century, and bears many traces of Arabian influence, mention is made of the use of saltpetre, *sal petrosum*, as a constituent of gunpowder. None of the Arabian alchemists appear to have been aware of the property of saltpetre deflagrating when mixed with a combustible body, and not until

[1] Groschuff, *Zeit. anorg. Chem.*, 1904, **40**, 1.

[2] For much interesting information concerning the early history of gunpowder, see Guttmann, *Monumenta Pulveris Pyrii* (Printed for the Author at the Artist's Press, Balham, London, 1906).

the thirteenth century do we find this clearly pointed out by Roger Bacon as follows:—[1] "Talis natura est (sal nitrum), quod si immediate ignitos carbones tangat, statim accensum impetu evolat."

This fact is strikingly shown when a mixture of twenty parts of nitre and three parts of charcoal is thrown into a red-hot crucible, vivid incandescence and a violet combustion being noticed:

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$

An intimate mixture of fifteen parts of saltpetre and five parts of sulphur also burns very brilliantly:

$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Detonating Powder, first described by Glauber, consists of a mixture of three parts of saltpetre, two parts of dry potassium carbonate, and one part of sulphur. When the mixture is heated in an iron spoon it first fuses and then explodes violently. In this reaction the sulphur forms potassium sulphide, which at the high temperature of the combustion is oxidised by the nitre, free nitrogen being evolved.

Powder of Fusion or *Baumé's Quick Flux*, also mentioned by Glauber, contains one part of nitre, one part of sulphur, and one of sawdust. This if set on fire burns with so much heat that a small silver coin exposed to it is rapidly melted.

174 *Gunpowder.*—Fire-arms appear to have been used in Florence in 1325, but field pieces were first employed by the English at the battle of Crécy in 1346.

Gunpowder consists of a mixture, in somewhat varying proportions, of charcoal, sulphur, and nitre. Its explosive power depends on the rapid combustion of the charcoal and sulphur at the expense of the oxygen of the nitre, and the sudden liberation of a large volume of gas, which occupies several hundred times the bulk of the solid powder. Hence gunpowder can burn in a closed space or under water, as it contains in itself the oxygen needed for the combustion. A singular fact which has been found to be true in practice is that the description of gunpowder which acts best is that which contains nearly two molecules of nitre to one atom of sulphur and three of carbon. Hence it was formerly believed that the decomposition which

[1] Breve breviarium de Dono Dei.

took place when powder was fired was a very simple one, represented by the following equation:

$$2KNO_3 + S + 3C = K_2S + N_2 + 3CO_2.$$

If this equation represents the decomposition which actually occurs, it follows that the most effective powder must be composed of:

Nitre	74·9
Carbon	13·3
Sulphur	11·8
	100·0.

The compositions of the gunpowders employed by different nations approach closely to these theoretical numbers; but in no case, as will hereafter be seen, are these numbers exactly adhered to. Indeed, the fact that the charcoal employed in the manufacture of gunpowder does not consist of pure carbon, but contains considerable quantities of hydrogen and oxygen, is sufficient to show that the above simple reaction cannot represent the real decomposition which occurs when powder is fired. In addition to this, however, Gay-Lussac and Chevreul proved long ago that, in addition to nitrogen and carbon dioxide, carbon monoxide is evolved in the firing of gunpowder, whilst the residue does not merely consist of potassium sulphide, but contains the carbonate, sulphate, and other salts.

We owe the first careful experimental investigation concerning the nature of the decompositions which occur when powder is fired to Bunsen and Schischkoff.[1] They proved that a very large number of salts, such as sulphate, thiosulphate, sulphide, and carbonate of potassium, are contained in the smoke and solid residue remaining after the powder has been fired; whilst many other gases, especially carbon monoxide, hydrogen, and sulphuretted hydrogen, besides carbon dioxide and nitrogen, are formed. In these experiments the powder was fired into a vacuum, and consequently some conditions as regards temperature and pressure which are met with in the practical use of gunpowder were not maintained. Linck repeated these experiments with a different kind of powder, and Karolyi analysed the products obtained by exploding small charges in shells inclosed in a vacuous space.

[1] *Phil. Mag.*, 1858 (4), **15**, 489.

Subsequently Abel and Noble[1] published the results of a very complete investigation on the products of combustion of powder fired under conditions similar to those which exist when it is fired in guns. The gunpowder operated upon included five kinds, viz., pebble powder, rifle large-grain (cannon powder), fine-grain powder, and rifle fine-grain powder, all English military powders, together with one spherical pellet powder of Spanish manufacture. The following table gives the complete analyses of the different powders employed:

	Pebble powder. Waltham Abbey.	Rifle large-grain (cannon powder). Waltham Abbey.	Rifle fine-grain. Waltham Abbey.	Fine-grain. Waltham Abbey.	Spanish spherical pebble powder.
Saltpetre . .	74·67	74·95	75·04	73·55	75·30
Potassium sulphate . .	0·09	0·15	0·14	0·36	0·27
Potassium chloride	—	—	—	—	0·02
Sulphur . . .	10·07	10·27	9·93	10·02	12·42
Charcoal: Carbon . .	12·12	10·86	10·67	11·36	8·65
Charcoal: Hydrogen.	0·42	0·42	0·52	0·49	0·38
Charcoal	14·22	13·52	14·09	14·59	11·34
Charcoal: Oxygen .	1·45	1·99	2·66	2·57	1 68
Charcoal: Ash . . .	0·23	0·25	0·24	0·17	0·63
Water	0·95	1·11	0·80	1·48	0·65

The quantities of gunpowder exploded in the several operations varied from 100 to 750 grams. The apparatus in which the charges were exploded consisted of a mild steel vessel of great strength, carefully tempered in oil. The charge to be exploded was placed in the chamber of this steel vessel, and the main orifice of the vessel was closed by a screw plug, called the firing-plug, which fitted into its place with great accuracy. In this firing-plug itself was a conical hole, also stopped by a plug, and through this passed two insulated platinum wires, by means of which the charge could be fired by electricity. Two other apertures were made in the chamber; one of these communicated with the arrangement for allowing the gases to escape; the other contained an apparatus for determining the pressure of the gases at the moment of explosion. The pressures actually observed varied from 1 to 36 tons on the square inch, the whole of the gaseous products remaining pent-

[1] *Phil. Trans.*, 1875, **165**, 49.

up in the cylinder under this enormous pressure. The results of this investigation may be shortly stated as follows:

(1) The composition of the *gas* furnished by the explosion of all the English powders is remarkably uniform, but under high pressures the carbon dioxide increases and the carbon monoxide decreases.

(2) The composition of the *solid* products exhibits a much greater variation.

(3) The decomposition which an average gunpowder undergoes when fired in a closed space cannot be represented by even a comparatively complicated chemical equation.

(4) The volume of the permanent gases, measured at 0° and 760 mm., furnished by combustion of one gram of powder in a closed vessel is about 280 c.c., and is therefore about 280 times the volume of the powder.

(5) When 1 gram of powder is burnt the solid products of combustion amount to 0·57 gram, and the permanently gaseous products 0·43 gram.

(6) The pressure of the products of combustion when the powder entirely fills the space in which it is fired is about 6,400 atmospheres, or 42 tons per square inch.

(7) The heat developed by the burning of 1 gram of powder is about 705 thermal units.

(8) The temperature of explosion is about 2,200° C.

The following tables give the analytical results obtained with three of the powders, including both the solid and gaseous products of combustion.

I. (Pebble); II. R. L. G. (Rifle Large Grain); III. F. G. (Fine Grain), each under two different pressures.

	Pebble. I.		R. L. G. II.		F. G. III.	
Pressure of explosion in tons per square inch . .	1·4	12·5	1·6	35·6	3·7	18·2
Percentage weight of solid products	56·12	55·17	57·22	57·14	58·17	58·08
Percentage weight of gaseous products	43·88	44·83	42·78	42·86	41·83	41·92

COMPOSITION BY WEIGHT (IN GRAMS) OF THE PRODUCTS OF EXPLOSION OF A GRAM OF POWDER AS FURNISHED BY THE ABOVE EXAMPLES.

	I.		II.		III.	
Potassium carbonate	0·3115	0·3098	0·3007	0·3755	0·3454	0·2499
thiosulphate . .	0·1163	0·0338	0·1166	0·0491	0·0308	0·1863
sulphate . . .	0·0843	0·0658	0·1171	0·0487	0·1409	0·1220
sulphide . . .	0·0416	0·1055	0·0230	0·0413	0·0298	—
thiocyanate . .	0·0005	0·0013	0·0000	0·0021	0·0001	0·0013
nitrate	0·0027	0·0011	0·0032	0·0011	0·0005	0·0011
oxide	—	—	—	—	—	0·0173
Ammonium sesquicarbonate . .	0·0009	0·0004	0·0003	0·0009	0·0009	0·0002
Carbon	—	—	0·0072	—	—	—
Sulphur	0·0034	0·0340	0·0041	0·0527	0·0333	0·0027
Total solid . .	0·5612	0·5517	0·5722	0·5714	0·5817	0·5808
Sulphuretted hydrogen	0·0134	0·0084	0·0166	0·0077	0·0154	0·0081
Oxygen	—	—	—	—	—	0·0006
Carbon monoxide .	0·0519	0·0473	0·0303	0·0356	0·0416	0·0258
Carbon dioxide . .	0·2577	0·2770	0·2597	0·2750	0·2512	0·2718
Methane	—	0·0012	0·0006	0·0015	—	0·0009
Hydrogen	0·0007	0·0005	0·0005	0·0003	0·0010	0·0005
Nitrogen	0·1151	0·1139	0·1201	0·1085	0·1091	0·1117
Total gaseous .	0·4388	0·4483	0·4278	0·4286	0·4183	0·4192

The total theoretic work of gunpowder is about 332,000 gram-metres per gram, or 486 foot-tons per lb. of powder.

A difference between the products of powder of large and small grain can be observed. The very small grain powders furnish decidedly smaller proportions of gaseous products than a large-grain powder, and this again smaller than a pebble powder. The most important solid products are found to consist of the following potassium salts: carbonate, sulphate, thiosulphate, and sulphide. The proportion of carbonate is much larger, and that of sulphate very much smaller, than was formerly believed to be the case.

POTASSIUM AND PHOSPHORUS.

175 *Normal Potassium Orthophosphate*, K_3PO_4, is formed, according to Graham, when phosphoric acid is ignited with an excess

of potassium carbonate. It is more general now to heat a mixture of phosphatic slag or naturally occurring calcium phosphate with powdered coke and potassium sulphate. It is readily soluble in water, and crystallises in small needles. The mono-acid salt, K_2HPO_4, does not readily crystallise, and the di-acid salt, KH_2PO_4, is obtained by adding phosphoric acid to a solution of potassium carbonate until the liquid after boiling is neutral to phenolphthaleïn. The salt is deposited in deliquescent tetragonal crystals, easily soluble in water, but insoluble in alcohol. It is employed in the manufacture of artificial fertilisers.[1]

Potassium Pyrophosphate, $K_4P_2O_7$.—When the mono-acid ortho-phosphate is ignited this salt is formed. It deliquesces on exposure, and is deposited in the form of fibrous crystals containing three molecules of water, when the solution is evaporated. The acid salt, $H_2K_2P_2O_7$, separates out as a white deliquescent mass when the normal pyro-salt is dissolved in acetic acid and alcohol added to the solution.

Potassium Metaphosphates.—These salts exist in a large number of polymeric modifications, which closely resemble the corresponding sodium salts (p. 267).

Potassium and Arsenic.

176 *Potassium Arsenide.*—Two arsenides of potassium, AsK_3 and As_4K_2, have been prepared by acting on a solution of potassium in liquid ammonia with arsenic, and heating the resulting compounds.[2]

Potassium Arsenite.—Arsenious oxide dissolves easily in an aqueous solution of potash, and if the minimum quantity of potash be employed, the compound $KAsO_2,H_3AsO_3$ may be obtained as a crystalline powder when the solution is mixed with alcohol. If this is warmed with a solution of potassium carbonate, potassium meta-arsenite, $KAsO_2$, is formed, and this when warmed with caustic potash yields potassium diarsenite, $K_4As_2O_5$, likewise precipitable by alcohol.

A solution of potassium arsenite is used in medicine under the name of Fowler's Solution. This solution is prepared by boiling one part of solid arsenious oxide with an equal weight of

[1] Meyer, *Zeit. angew. Chem.*, 1905, **18**, 1382.
[2] Hugot, *Compt. rend.*, 1899, **129**, 603.

potassium carbonate in distilled water, and diluting the clear liquid so as to form 90 parts of solution.

Normal Potassium Arsenate, K_3AsO_4, is prepared by adding an excess of caustic potash to arsenic acid. On evaporation it is deposited in the crystalline form (Graham). Monohydrogen potassium arsenate, K_2HAsO_4, crystallises with difficulty, but the dihydrogen salt, KH_2AsO_4, can be obtained in large crystals. This last salt was known as *Macquer's arsenikalisches Mittelsalz*, and was formerly prepared by deflagrating equal parts of arsenious oxide and nitre, dissolving in water, and leaving the solution to crystallise. These crystals are isomorphous with di-hydrogen potassium phosphate, and likewise turn blue litmus paper red.

Potassium and Boron.

177 *Potassium Metaborate*, KBO_2.—When boric acid and potassium carbonate (or any other potassium salt containing a volatile acid) are fused together in the proper proportions, the above salt is obtained. It is sparingly soluble in water, and is deposited in small monoclinic crystals, possesses an alkaline reaction, and absorbs carbonic acid from the air with formation of *potassium pyroborate* or *tetraborate*. This latter substance is obtained by adding caustic potash to a solution of boric acid until the liquid attains an alkaline reaction. It is easily soluble, crystallises in hexagonal prisms having the formula $K_2B_4O_7,5H_2O$, and possesses a faint alkaline taste. If hot solutions of boric acid and potassium carbonate be mixed together, in the proportion of one molecule of the former to two molecules of the latter, glittering rhombic crystals of *potassium triborate*, $2KB_3O_5,5H_2O$, separate out, and when a hot solution of caustic potash is saturated with boric acid, rhombic pyramids of *potassium pentaborate*, $KB_5O_8,4H_2O$, are deposited.

Potassium Perborate, $KBO_3,4H_2O$, is precipitated by alcohol from a solution of the borate in hydrogen peroxide, and has the characteristic oxidising properties of this class of salts (Vol. I., p. 729; this vol., p. 273).

Potassium and Carbon.

178 *Potassium Carbide*, K_2C_2, closely resembles the sodium compound (p. 273), and is prepared in a similar manner. The compound with acetylene, C_2K_2,C_2H_2, crystallises in brilliant silky, rhombohedral lamellæ.[1]

[1] Moissan, *Compt. rend.*, 1898, **126**, 302; 1898, **127**, 911.

Normal Potassium Carbonate, K_2CO_3.—This salt, well-known under the name of potashes, was originally obtained solely from the ashes of wood and other land plants, as the name implies, boiled in pots. Even to the present day this compound is sometimes obtained according to the old process, especially in Canada, North America, Moravia, the Steppes of Southern Russia, Hungary, and other districts where wood is plentiful. The ashes are lixiviated in wooden tubs, and the dark brown lye thus obtained evaporated to dryness or to the point of crystallisation, and the residue calcined in a reverberatory furnace to remove organic matter. The crude product has usually a red, yellow, or green colour, due to the presence of iron or manganese, and also contains potassium chloride, sulphate and silicate, as well as sodium salts, and, where caustic lime is added, as in the preparation of American potash, considerable quantities of caustic potash; the latter may be converted into carbonate by calcining the crude ash with sawdust. To purify the crude ash it is redissolved in two parts of boiling water, the filtered solution is allowed to stand for some days, then poured off from separated salts, consisting chiefly of potassium sulphate, and the clear solution evaporated till the salt commences to crystallise out. After cooling, it is drained and washed with small quantities of water to remove the adherent mother liquor. To the white salt thus obtained the name *pearl-ash* is given.

Owing to the high price of potashes and the gradual extinction of forests, and in consequence of this alkali being a substance largely needed in manufacturing processes, other sources of potassium compounds have been sought. The suggestion has frequently been made that felspar and other silicates of potash should be employed for the purpose, and this proposition seems a very plausible one, inasmuch as it is by the slow decomposition of these silicates that all fruitful soils obtain their potash salts. Hitherto, however, it has not been found possible to obtain potash commercially from this source, and fortunately other richer sources of potassium compounds have been discovered. Amongst these the first to be noted is that from the manufacture of beet-root and cane sugar. Beet-root is a potash plant, its ash being particularly rich in potassium compounds. The first attempt to obtain potash from this plant was made by incinerating the leaves. This process, however, did not prove satisfactory, and the molasses or

uncrystallisable sugar, which contains large quantities of potash salts, is now evaporated, and either heated in a furnace to remove the organic matter, or distilled and the nitrogen recovered in the form of ammonia and cyanides. In either case a residue of potash salts and carbon is left, from which the salts are removed by lixiviation.

Another remarkable source of potash is sheep-wool. It has already been mentioned that sheep withdraw a considerable quantity of potash salts from the soil. Chevreul first pointed out that the sweat or suint of sheep contains no less than one-third of its weight of potash salts. The brown liquors in which the wool has been washed are evaporated to dryness, and the solid residue calcined in retorts, by which means ammonia and a gas used for illuminating purposes are evolved; the residual mixture of charcoal and alkaline salts is again lixiviated, and treated in a similar way to the case already described.

Potashes are also manufactured from potassium sulphate, which is obtained in considerable quantity from the Stassfurt beds, from sea-water, by heating potassium chloride with sulphuric acid, and in the manufacture of dichromate. For the purpose of converting the sulphate into the carbonate it is heated in a reverberatory (black-ash) furnace with the requisite quantity of limestone and coal, the process being worked exactly according to Leblanc's process for obtaining carbonate of soda from salt-cake (p. 288).

The greater part of the potassium carbonate which is made from the Stassfurt salt is manufactured by the magnesia-potash process from potassium chloride. This depends on the fact that in the presence of magnesium carbonate, potassium chloride is decomposed below 24° by carbon dioxide, with formation of an insoluble double salt, $KHCO_3,MgCO_3,4H_2O$, and magnesium chloride. The precipitated salt is washed and then decomposed by warm water, or by magnesium hydroxide below 20°, and the solution of potassium carbonate is evaporated and calcined.[1]

In order to prepare chemically pure potassium carbonate, it was customary formerly to employ pure cream of tartar (hydrogen potassium tartrate), which was heated in covered iron crucibles. A mixture of carbon and potassium carbonate was thus obtained, and by lixiviating the residue with water

[1] German Patents 135329; 143408; 143409; 157354. Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 791.

and evaporating the solution in a silver basin the pure salt was deposited. This salt even now retains the name of salt of tartar. Instead of the expensive tartar it is now customary to employ the much cheaper hydrogen potassium carbonate or bicarbonate of potash, which can be easily prepared in the pure state, and which on heating yields water, carbon dioxide, and potassium carbonate:

$$2KHCO_3 = H_2O + CO_2 + K_2CO_3.$$

When prepared on the manufacturing scale, the carbon dioxide which is evolved is made use of for the preparation of a fresh portion of bicarbonate.

Pure potassium carbonate occurs either in the form of a white granular powder, or as a white solid mass, which possesses a strong alkaline reaction, and has an alkaline and slightly caustic taste. It has the sp. gr. 2·29, melts at 879°, and then loses a small quantity of carbon dioxide; it is converted into caustic potash and carbon dioxide at a red heat in a current of steam or hydrogen. At a white heat it is volatilised. It is extremely hygroscopic and very soluble in water, and when exposed to the air it soon deliquesces to an oily liquid which received the name of "oleum tartari per deliquium." One hundred parts of water dissolve the following quantities of salt[1]:—

0°	26°	40°	60°	80°
105	113·5	117	127	140 parts.

At 135°, the boiling point of the saturated solution, 100 parts of water dissolve 205 parts of the salt. The hydrate which is stable in contact with water from −6·8° to 135° contains $2H_2O$.[2] For the specific gravity of solutions of this salt, Gerlach's tables may be consulted.[3] When the concentrated solution is allowed to stand, monoclinic crystals, possessing a glassy appearance and having the composition $2K_2CO_3,3H_2O$, are deposited. These on heating to 100° fall to a white powder having the composition, K_2CO_3,H_2O, and this at 130° loses all its water.

Potassium carbonate is largely used in the manufacture of soft soap, potassium ferrocyanide and chromate, and crystal glass.

[1] Meyerhoffer, Landolt-Börnstein, *Physikalisch-Chemische Tabellen* (1905), p. 542.

[2] See also Lescoeur, *Bull. Soc. Chim.*, 1897 (3), **17**, 18.

[3] *Zeit. anal. Chem.*, 1869, **8**, 279.

Hydrogen Potassium Carbonate, $KHCO_3$.—This salt, also known as potassium bicarbonate, is obtained by passing carbon dioxide through a concentrated solution of the normal salt, when the bicarbonate, which is much less soluble, crystallises out. Another process is to pass a current of carbon dioxide over the slightly moistened purified potashes, the product being recrystallised from warm water. It forms large, transparent crystals belonging to the monoclinic system, which possess a saline taste and a slightly alkaline reaction. 100 parts of water dissolve at 10° 27·7 parts, and at 60°, 60 parts of the salt. When the solution is boiled carbon dioxide is given off, and when the dry salt is heated to 190° it is completely decomposed into the normal carbonate, carbon dioxide, and water.

Potassium Percarbonate, $K_2C_2O_6$, has already been described (Vol. I., p. 825).

Potassium Sulphocarbonate, K_2CS_3, is prepared by the interaction of carbon disulphide and potassium sulphide. The salt has a yellow colour, and is readily soluble in water.

Potassium Cyanide, KCN.—Commercial potassium cyanide was formerly prepared according to Liebig's method as follows. Eight parts of dry ferrocyanide of potassium (for the manufacture of which see under Iron) are melted in an iron crucible together with three parts of potassium carbonate:

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KOCN + CO_2 + Fe.$$

As is seen from this equation, the cyanide thus prepared contains cyanate; for some purposes this is of no consequence. A purer product can be obtained by heating the dry ferrocyanide to a bright red heat:

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

To avoid the loss of cyanogen which thus takes place in both these reactions it is now usual to heat the completely dehydrated ferrocyanide with metallic sodium:

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The resulting mixture of potassium and sodium cyanides is known commercially as potassium cyanide. A large amount of potassium cyanide is now made by Beilby's process, which consists in treating a fused mixture of potassium carbonate and charcoal with ammonia, the product being a molten cyanide of high strength, which is filtered from the small amount of

insoluble matter present and is then cast in moulds, thus yielding massive crystalline cakes of pure white cyanide.[1] It is also manufactured on a commercial scale from the waste product known as "Schlempe" of the beet sugar refineries. The process is one of destructive distillation. Chemically pure potassium cyanide is best prepared by passing the vapour of hydrocyanic acid into an alcoholic solution of potash, the salt then separating out as a white, crystalline powder.

Potassium cyanide has a sharp bitter taste; it is exceedingly soluble in water, and dissolves slightly in cold, and somewhat more readily in hot, alcohol. When the concentrated aqueous solution of the salt is allowed to evaporate over strong sulphuric acid, it deposits crystals in the form of regular octahedra. Potassium cyanide is readily fusible, and on cooling solidifies in cubes. The weakest acids, even carbonic acid, decompose the salt with evolution of hydrocyanic acid. The salt is, moreover, partially hydrolysed in its aqueous solution, which possesses an alkaline reaction and always smells of hydrocyanic acid. It is itself as poisonous as the acid.

Potassium cyanide is used in very large quantities in the Macarthur-Forrest process for recovering the last portions of gold from the tailings of the gold mines[2] (see Gold); in the laboratory it is also used as a reducing agent. This is due to the fact that when in the fused state it withdraws oxygen from many oxides and is converted into potassium cyanate. When heated with nitric acid or potassium chlorate violent explosions occur. Potassium cyanide and sulphur when melted together combine directly, forming potassium thiocyanate. This compound is also formed when the cyanide is heated with some metallic sulphides.

Potassium Cyanate, KCNO or CO:NK, is prepared by heating four parts of very carefully dried potassium ferrocyanide and three parts of fused potassium dichromate in an iron dish, and extracting the product with hot 80 per cent. methylated spirit. It crystallises on cooling in transparent plates, which are readily soluble in water and alcohol, the aqueous solution gradually decomposing into ammonia and potassium hydrogen carbonate:

$$KCNO + 2H_2O = NH_3 + KHCO_3.$$

[1] Beilby, "Advances in Chemical Industry during the Nineteenth Century." *Proc. Roy. Phil. Soc.*, Glasgow, 1904.

[2] *J. Soc. Chem. Ind.*, 1890, **9**, 270; Maclaurin, *Journ. Chem. Soc.*, 1893, **63**, 724; 1895, **67**, 199.

The cyanate can also be readily prepared by the electrolytic oxidation of a solution of potassium cyanide containing caustic potash.[1] Potassium cyanate is employed in the preparation of certain organic compounds.

Potassium Thiocyanate, KCNS or CS:NK, is formed by the direct union of potassium cyanide and sulphur, but is usually prepared by gently heating a mixture of 46 parts of dry potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur. The mass after cooling is extracted with boiling alcohol, and the salt crystallises from the cooled solution in long striated prisms, which readily melt when heated and deliquesce in moist air. One hundred parts of water dissolve 217 parts of the salt at 20°, a considerable amount of heat being absorbed; thus if 500 grams of the salt be mixed with 400 grams of water the temperature of the mass sinks to −20°; hence the salt has been used as a refrigerant.

It melts at 172°, and on heating to 430° becomes coloured blue, the blue colour changing to white again on cooling.[2]

This salt occurs in minute amounts in human saliva.

Potassium and Silicon.

179 *Potassium Silicates.*—When silica is fused with potassium carbonate, carbon dioxide is evolved, and according to the proportions of the two substances employed, the temperatures and the duration of heating, the silicates K_2SiO_3, $K_4Si_3O_8(2K_2O,3SiO_2)$, and $K_8Si_3O_{10}(4K_2O,3SiO_2)$ are obtained.[3] Attempts to obtain the orthosilicate K_4SiO_4 have all been unsuccessful, and in all probability it does not exist.

Potassium Metasilicate, K_2SiO_3, obtained by fusing equal molecular proportions of silica and potassium carbonate, forms a glassy mass which deliquesces on exposure to moist air. It also absorbs carbonic acid from the air, and is gradually transformed into a transparent jelly which in time shrinks together, and after some weeks becomes hard enough to scratch glass. It is probable that opal and flint are formed in a similar manner (Kuhlmann). Van Helmont was aware that the substance obtained by fusing silica with an excess of alkali became liquid on exposure to air, and Glauber termed this *liquor silicum*.

[1] Paternò and Pannain, *Gazz.*, 1904, **34**, ii., 152.

[2] Paternò and Mazzucchelli, *Atti R. Accad. Lincei*, 1907, [v.], **16**, i., 465.

[3] Scheerer, *Annalen*, 1860, **116**, 149.

Soluble potash glass is prepared in a similar manner to soluble soda glass (p. 278), and closely resembles it in properties. It has been used for a variety of purposes, but its place has mostly been taken by the cheaper soda glass.

Potassium silicofluoride, K_2SiF_6, is obtained when hydrofluosilicic acid is brought into contact with a solution of a potassium salt. When the acid is added in small quantities no precipitate is observed to form, but soon the liquid begins to exhibit iridescent colours, and after a time the insoluble potassium fluosilicate separates out as a semi-transparent mass. After washing with water and drying, the salt is obtained as a fine white powder sparingly soluble in cold, though easily soluble in hot, water. By slow cooling it may be obtained in the form of bright octahedra, which sometimes show cubic faces (Marignac).

Detection and Estimation of Potassium and its Compounds.

180 The best indication of the presence of potassium compounds is the violet colour which they impart to the non-luminous flame. This tint is, however, not seen if even a small quantity of a sodium compound is present, and it is then necessary to examine the flame by means of the spectroscope. The spectrum thus obtained is that of the metal itself and contains only two characteristic lines:—viz., the double line Kα (7697 and 7663), in the outermost red, approaching the ultra red rays and below the dark line A of the solar spectrum; and a second line Kβ (4044), situated far in the violet rays, towards the other end of the spectrum, also identical with a dark solar line. Owing to the position of the two lines, Kα and Kβ, both situated near the limit at which our eyes cease to be sensitive to the rays, this reaction for potassium is not very sensitive, but $\frac{1}{1000}$ of a milligram can be readily detected. The absorption spectrum of potassium has been mapped by Roscoe and Schuster.[1] It is totally different from the emission spectrum just described, being a channelled space spectrum. Observed at a low temperature, the green-coloured vapour exhibits a well-marked series of

[1] *Proc. Roy. Soc.*, 1874, **22**, 362.

bands, one group in the red (α) and two groups (β and γ) at each side of the sodium line being seen. These bands are all shaded off towards the red, and in general appearance resemble those of the iodine spectrum.

In order to detect and estimate soluble potassium compounds they must be precipitated either as the perchlorate, the phosphotungstate, the acid tartrate, or the chloroplatinate K_2PtCl_6.

Potassium may be detected microchemically by the yellow precipitate or coloration produced with sodium cobaltinitrite and acetic acid,[1] and the same reagent has been proposed for its estimation.[2] Cunningham and Perkin have, however, shown that the method is not reliable.[3]

For the separation of this metal from sodium and for its quantitative estimation, an excess of chloroplatinic acid, H_2PtCl_6, is added to the mixed chlorides; the liquid is then evaporated on the water-bath, and the cooled residue mixed with strong alcohol, in which the excess of chloroplatinic acid and the sodium double salt easily dissolve. The potassium double salt is then collected, dried, and weighed, or its amount estimated indirectly from the amount of platinum or chlorine which it contains. Potassium may also be estimated by adding perchloric acid and alcohol to the concentrated solution, the precipitated potassium perchlorate being washed with a mixture of alcohol and water, dried, and weighed. The perchlorate method is now usually employed for the assay of potassium salts.

The mixed chlorides of potassium and sodium can also be weighed, and then converted into sulphates by treatment with strong sulphuric acid, and the weight of these determined. From these data the amount of potassium (x) and of sodium (y) present can readily be calculated when the molecular weights of the several salts are known. Thus:

K = 39·10	Na = 23·00	K_2 = 78·20	Na_2 = 46·00
Cl = 35·46	Cl = 35·46	SO_4 = 96·07	SO_4 = 96·07
74·56	58·46	174·27	142·07

[1] Macallum, *Journ. Physiol.*, 1905, **32**, 95.
[2] Adie and Wood, *Journ. Chem. Soc.*, 1900, **77**, 1076.
[3] *Journ. Chem. Soc.*, 1909, **95**, 1562.

If A represent the weight of the mixed chlorides, and B that of the mixed sulphates, we have :

$$A = \frac{74{\cdot}56}{39{\cdot}10}x + \frac{58{\cdot}46}{23{\cdot}00}y$$

$$B = \frac{174{\cdot}27}{78{\cdot}20}x + \frac{142{\cdot}07}{46{\cdot}00}y$$

Hence the values of x and y can be readily obtained.

A similar result may be obtained by simply ascertaining the amount of chlorine present in the mixed chlorides by titration with silver nitrate solution, but neither of these indirect methods is susceptible of great accuracy.

The atomic weight of potassium was determined by Stas. As a mean of eight experiments he found that 100 parts of potassium chlorate yielded 60·846 parts of potassium chloride on ignition. Moreover, 69·103 parts of potassium chloride were needed, as a mean of nineteen experiments, to precipitate 100 parts of silver from solution : and 100 parts of silver, as a mean of seven experiments, gave 132·8445 parts of silver chloride. These experiments give the number 38·85 as the mean for the atomic weight of potassium, the number 35·18 for that of chlorine, and the number 107·12 for that of silver when H = 1 (or K = 39·15, Cl = 35·45, and Ag = 107·93, when O = 16).

A closely agreeing result has been obtained by the analysis of the chloride by Archibald,[1] who found that 100 parts of silver were precipitated as chloride by 69·114 parts of potassium chloride, and that 100 of silver chloride were produced by 52·028 of potassium chloride. Finally, Richards and Staehler[2] have carefully analysed potassium chloride prepared from potassium nitrate, and have found the ratios KCl : Ag = 69·1072 : 100 ; KCl : AgCl = 52·0118 : 100. The atomic weight of potassium is therefore 38·821 when Ag = 107·12, and Cl = 35·207 ; or 39·114 when Ag = 107·93, and Cl = 35·473.

The international atomic weight of potassium (1913) is 39·10.

[1] *Trans. Roy. Soc., Canada* (2), **10**, iii., 47.

[2] *Ber.*, 1906, **39**, 3611.

RUBIDIUM. Rb = 85·45.

181 In the year 1860 Bunsen [1] announced the discovery by means of spectrum analysis of a new alkali metal, to which he gave the name of *Cæsium*, and in 1861 he discovered by the same method a second new alkali metal, and to this he gave the name *Rubidium*.

These two metals and their compounds possess so close a resemblance, and at the same time give reactions so similar to those of potassium, that they cannot be distinguished either from the well-known alkali or from one another by any of the common wet reactions or blowpipe tests. The only means by which their presence can be readily detected is by their spectrum reactions, and these are so delicate and so characteristic that they serve for the certain recognition of the minutest trace of these two new bodies, whether present alone or mixed with the other alkalis. The metals were first met with by Bunsen in the waters of Dürkheim in the Palatinate, and in the mineral petalite. In these, however, they are contained in such small quantity that, although their presence can be easily recognised in a few drops of the water or in a few grains of the mineral, it was requisite to boil down 40 tons of the water, and to work up 150 kilograms of the mineral, in order to obtain enough of the new metals to serve for the investigation of their compounds.

The following extract from Bunsen and Kirchhoff's second memoir on Spectrum Analysis [2] gives a clear idea of the method by which the presence of the two new metals was first detected:

"If a drop of the mother-liquor of the Dürkheim water be brought into the flame of the spectrum apparatus, the characteristic lines of sodium, potassium, lithium, calcium, and strontium are at once seen. If the lime, strontia, and magnesia be separated according to well-known processes, and if the residual alkali bases in the form of nitrates be washed out with alcohol, and the lithium removed as completely as possible by precipitation with carbonate of ammonium, a mother-liquor is obtained which in the spectrum apparatus shows the lines of sodium, potassium, and lithium, but, besides these, two splendid

[1] *Berlin Akad. Ber.*, May 10, 1860.
[2] *Phil. Mag.*, 1861, (4), 22, 330.

blue lines situated close together, and almost coinciding with the blue strontium line Srδ.

"As no known elementary body produces two blue lines in this portion of the spectrum, we may consider the existence of this hitherto unknown alkali element as thus placed beyond doubt.

"The facility with which a few thousandths of a milligram of this body may be recognised by the bright blue light of its incandescent vapour, even when mixed with large quantities of the more common alkalis, has induced us to propose for it the name *Cæsium* (and the symbol Cs), derived from the Latin *cæsius*, used to designate the blue of the clear sky.[1]

"If Saxony lepidolite be treated by any of the known plans for separating the alkalis from the other constituents, and if the solution of the alkalis thus obtained be precipitated with dichloride of platinum, an abundant precipitate is formed, which, when examined in the spectrum apparatus, shows only the bright potassium lines. If this precipitate be repeatedly washed with boiling water, and the residual salt occasionally examined in the apparatus, two splendid violet lines, lying between the strontium line Srδ and the blue potassium line Kβ, will be noticed on the gradually fading continuous background of the potassium spectrum. These new lines increase in brilliancy as the washing is continued, and a number more appear in the red, yellow, and green portions of the spectrum.

"None of these lines belong to any previously known body. Amongst them are two which are especially remarkable as lying beyond Fraunhofer's line A and the potassium line Kα coincident with it, and therefore situated in the outermost portion of the red solar rays. Hence we propose for this new metal the name *Rubidium* (and the symbol Rb), from the Latin *rubidus*, which was used to express the darkest red colour." [2]

Since this discovery, rubidium has been shown to be widely distributed (see also p. 162), generally accompanying the other alkalis, but in very minute quantities. Rubidium occurs in many minerals, such as lepidolite and triphylite, in Vesuvian leucite, in the porphyrites of the Palatinate, in mica, in

[1] Aulus Gellius in his *Noctes Atticæ*, ii., 26, quotes Nigidius Figulus as follows: "Nostris autem veteribus cæsia dicta est, quæ a Græcis γλαυκῶπις ut Nigidius ait, de colore cœli quasi cœlia."

[2] Aulus Gellius, *Noctes Atticæ*, ii., 26. "Rubidus autem est rufus atrior et nigriore multo inustus."

Stassfurt carnallite,[1] and in orthoclase. It is also present in nearly all iron ores, except red hæmatite, in many meteorites and in some aluminous minerals, such as bauxite and shale.[2]

The following is the analysis of the lepidolite from Rozena in Moravia in which Kirchhoff and Bunsen first discovered rubidium:—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Rb_2O.	Cs_2O.	Li_2O.	LiF.
50·32	28·54	0·73	1·01	0·51	0·24	trace	0·70	0·99

NaF.	KF.	H_2O.
1·77	12·06	3·12

A large number of brine springs and mineral waters also contain this alkali. Thus the hot springs of the Ungemach contain in one litre 1·3 milligrams of chloride of rubidium (Bunsen); the mineral water of Bourbonne-les-Bains contains 18·7 milligrams of the same salt, and 32·5 milligrams of cæsium chloride.

The celebrated waters of Ems, Kissingen, Nauheim, Selters, Vichy, Wildbad-Gastein, and many others contain rubidium, and some of them also cæsium compounds. Rubidium has been found in sea-weed and in sea-water (Sonstadt),[3] and also in the mother-liquors (bitterns) from the salterns of Villefranche (Grandeau). Rubidium salts are also widely met with in the vegetable kingdom. Beet-root takes up these salts from the soil, and in the saline residue obtained by calcining the fermented molasses considerable quantities of rubidium salts are contained. Thus 100 parts of the saline residue contain 0·18 part of chloride of rubidium (Grandeau). It has also been found in samples of tobacco grown in the most distant quarters of the globe—such as Algiers, Havana, Kentucky, France, and Macedonia. Rubidium likewise occurs in several kinds of coffee and tea (Grandeau): in the ash of the oak, *Quercus pubescens*, in that of beech trees grown on a basaltic soil, in crude cream of tartar, and in potashes from various sources. Plants cannot, however, absorb rubidium salts in place of potassium salts, and they die if these latter are not present (Lucanus).

Mode of Preparation of Rubidium Compounds.—According to Bunsen, the best source of rubidium is the saline residue left

[1] Feit and Kubierschky, *Chem. Zeit.*, 1892, **16**, 335.

[2] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533, 547; *Sci. Proc. Roy. Dublin Soc.*, 1898, N.S., **8**, 703.

[3] *Chem. News*, 1870, **22**, 25, 44.

from the preparation of lithium salts from Saxon lepidolite. This consists of the chlorides of sodium, potassium, and lithium, and traces of the chlorides of cæsium and rubidium. The separation of these metals is based upon the fact that their chlorides form double chlorides with platinic chloride, which are more insoluble than the corresponding potassium double chloride. One kilogram of the saline mixture is dissolved in 2·5 kilograms of water, and the cold liquid precipitated by a solution of thirty grams of platinum in aqua regia. The precipitate, having settled down, is collected and boiled twenty-five times successively with small quantities of water, in all about 1·5 kilograms, the liquid in each case being added to the solution of the original salt. A fresh precipitate is then formed, this is again washed and treated as the first, and when the above series of operations has been repeated seven or eight times the rubidium is found to be nearly all extracted. Each of the platinum precipitates is then dried, the platinum reduced by hydrogen, and the alkali chlorides dissolved in water. In this way 125 grams of rubidium chloride are obtained, containing three or four per cent. of chloride of potassium, and a little chloride of cæsium. By a repetition of the precipitation and washing of the platinichloride this quantity of potassium impurity can be so completely removed that the well-known red potassium line (Kα) is not seen with a spectroscope when some of the salt is held in the flame (Bunsen).

Another method consists in decomposing lepidolite with sulphuric acid, recrystallising the alums of potassium, cæsium, and rubidium which are formed, decomposing by baryta, treating the alkaline solution with carbon dioxide and converting into the oxalates. These salts are then fractionally crystallised, the potassium salt being the least soluble.[1]

The most important source for the preparation of rubidium salts is the mother-liquor left over in the manufacture of potassium chloride from carnallite, which contains rubidium carnallite, $RbCl.MgCl_2$; by the addition of aluminium sulphate the alum is produced, and by fractional crystallisation the pure rubidium compound can be obtained. The solubilities of the alums (in grams per 100 grams water) are as follows:

Potash Alum.	Rubidium Alum.	Cæsium Alum.
13·5	2·27	0·619

[1] Formánek, *Oesterr. Chem. Zeit.*, 1899, **2**, 309.

Numerous other methods for the separation of rubidium and cæsium from potassium have been proposed; amongst these may be mentioned precipitation with stannic chloride,[1] which converts them into the sparingly soluble stannic chlorides $2RbCl,SnCl_4$, and $2CsCl,SnCl_4$; conversion into the alums, both of which are only slightly soluble in water, and still less so in a solution of potash alum[2]; and conversion into the dichloro-iodides, which are much less soluble than the corresponding potassium compounds.[3]

To separate rubidium from cæsium, advantage is taken of the different solubilities of the sparingly soluble salts of the two metals. The platinichlorides do not give good results, but the alums, $Rb_2Al_2(SO_4)_4,24H_2O$ and $Cs_2Al_2(SO_4)_4,24H_2O$, have been successfully employed, the former being about four times as soluble as the latter.[4] The *hydrogen tartrates*, $RbHC_4H_4O_6$ and $CsHC_4H_4O_6$, may also be used, the latter being the more soluble,[5] and the chlorides may be precipitated by hydrogen chloride, the cæsium salt being the more soluble (Archibald).

The best method of separation is that of Godeffroy, which consists in the addition of antimony trichloride to a solution of the chlorides in concentrated hydrochloric acid, when the double cæsium antimony chloride, $3CsCl,2SbCl_3$, is precipitated, but not the rubidium salt.[6] This method is well adapted for obtaining pure cæsium salts, but not for removing the last traces of cæsium from rubidium salts.

182 Metallic rubidium is prepared in an analogous manner to potassium by heating a mixture of the carbonate and charcoal (obtained by the ignition of the hydrogen tartrate) to whiteness in an iron tube, and is also obtained by heating the carbonate or hydroxide with magnesium,[7] the hydroxide with aluminium, rubidium aluminate being then also formed,[8] or the chloride with metallic calcium.[9]

[1] Feit and Kubierschky, *Chem. Zeit.*, 1892, **16**, 335.

[2] Redtenbacher, *J. pr. Chem.*, 1865, **94**, 442; Setterberg, *Annalen*, 1882, **211**, 100.

[3] Wells, *Amer. Chem. J.*, 1901, **26**, 265; Archibald, *Journ. Chem. Soc.*, 1904, **85**, 776.

[4] Redtenbacher, *loc. cit.*; Godeffroy, *Annalen*, 1876, **181**, 176.

[5] Allen, *Amer. J. Sci.*, 1862, (2), **34**, 367.

[6] *Ber.*, 1874, **7**, 375; 1895, **8**, 9; *Annalen*, 1876, **181**, 176; Muthmann, *Ber.*, 1894, **26**, 1019, 1425.

[7] *Ber.*, 1890, **23**, 51; Erdmann and Köthner, *Annalen*, 1896, **294**, 55.

[8] Beketoff, *J. Russ. Chem. Phys. Soc.*, 1888, 363.

[9] Hackspill, *Compt. rend.*, 1905, **141**, 106.

It is a silver-white metal of specific gravity 1·52, which at −10° is still soft and wax-like, melts at 38·5°, boils at 696° (Ruff and Johannsen), and emits at incipient redness a blue coloured vapour. Like potassium, it appears to form an explosive compound with carbon monoxide. When thrown on water rubidium burns like potassium.

COMPOUNDS OF RUBIDIUM.

183 These compounds as a rule present the greatest similarity to those of potassium and ammonium, and are isomorphous with them (see p. 218).

Rubidium Oxides.—Rubidium *monoxide*, Rb_2O, is obtained by partial oxidation of the metal and subsequent distillation of the excess of rubidium. It forms light yellow, transparent crystals, which melt at 250° and react vigorously with water. The *peroxide*, Rb_2O_2, is obtained by heating rubidium in excess of oxygen; it is a light-yellow, crystalline body. When rubidium is heated for a long time in excess of oxygen, the *tetroxide*, Rb_2O_4, is produced. It is a yellowish-brown, crystalline substance, which melts between 600° and 650° when heated in oxygen. When heated in vacuum to 600° oxygen is given off, and a blackish mass, the *trioxide*, Rb_2O_3, is left behind. Rb_2O_2 and Rb_2O_4 can also be obtained by the action of oxygen on rubidium dissolved in liquid ammonia at −50°.[1]

Rubidium Hydroxide, RbOH, is best prepared by adding baryta water to a solution of rubidium sulphate. It forms a greyish-white, deliquescent mass, melts at a red heat and is volatile in the flame of a Bunsen burner. It is a stronger base than potassium hydroxide.

Rubidium Hydride, RbH, forms colourless, prismatic needles of sp. gr. 2. It decomposes below 300° in vacuo into its elements.[2]

Rubidium Chloride, RbCl.—Rubidium takes fire in chlorine gas, burning with a bright light. Chloride of rubidium crystallises in glittering cubes which melt at 710°. 100 parts of water dissolve 84·4 parts of the salt at 10°, and 138·9 parts at 100°.

[1] Rengade, *Compt. rend.*, 1906, **142**, 1533; 1907, **145**, 236; *Ann. Chim. Phys.*, 1907, **11**, 348.

[2] Moissan, *Compt. rend.*, 1903, **136**, 587.

The *bromide* and *iodide* are very similar to the corresponding potassium salts.

The rubidium halides unite with a large number of metallic chlorides forming double salts which for the most part crystallise well. Rubidium also forms compounds with a larger number of halogen atoms much more readily than potassium, the compounds being also more stable. The following are known, and are all crystalline: $RbBr_3$, $RbClBr_2$, $RbCl_2Br$, RbI_3, $RbBr_2I$, $RbCl_2I$, $RbClBrI$, $RbCl_4I$.[1] The solid polyiodides RbI_7 and RbI_9 exist at 25°, but have not been prepared pure.[2]

Rubidium Chlorate, $RbClO_3$, is obtained by the double decomposition of rubidium sulphate and barium chlorate. It crystallises in small prisms which taste like potassium chlorate, and of which 2·8 parts dissolve in 100 parts of water at 4·7°, and 5·1 parts at 19°.

Rubidium Perchlorate, $RbClO_4$, is a granular powder consisting of glittering microscopic crystals belonging to the rhombic system. When heated below redness it decomposes into rubidium chloride and oxygen. 100 parts of water dissolve 1·085 parts of the salt at 21·3°.

Rubidium Sulphides.[3]—The *monosulphide*, $Rb_2S,4H_2O$, is obtained by the action of hydrogen sulphide on a solution of the hydroxide, and precipitation with alcohol. The *tetrasulphide*, $Rb_2S_4,2H_2O$, is obtained by adding the calculated quantity of sulphur to a solution of the monosulphide. When an excess of sulphur is added to a solution of the monosulphide, and the mixture is heated in an atmosphere of hydrogen, the *pentasulphide*, Rb_2S_5, is produced. The pentasulphide when heated in an atmosphere of nitrogen is converted into the *trisulphide*, Rb_2S_3, but when heated in an atmosphere of hydrogen the *disulphide* is formed.

Normal Rubidium Sulphate, Rb_2SO_4, exists as large rhombic crystals which taste like potassium sulphate. 100 parts of water dissolve 42·6 parts of this salt at 10°, and 81·8 at 100°.

Rubidium Selenate, Rb_2SeO_4, has the density 3·9: 100 parts of water dissolve 158·9 parts of the salt at 12° (Tutton).

Rubidium Nitrate, $RbNO_3$, crystallises in needles or prisms,

[1] *Amer. J. Sci.* (3), 1892, **43**, 475; **44**, 42; 1893, **46**, 88, 269; *Amer. Chem. J.*, 1896, **18**, 847; *Zeit. physikal. Chem.*, 1899, **28**, 523.

[2] Abegg, *Zeit. anorg. Chem.*, 1906, **50**, 403.

[3] Biltz and Wilke-Dörfurt, *Ber.*, 1905, **38**, 123; *Zeit. anorg. Chem.*, 1906, **50**, 67.

and is very soluble in water, 100 parts of which dissolve at 0° 19·5, and at 100° 452 parts of this salt. It can be distinguished from nitre, inasmuch as it readily dissolves in concentrated nitric acid.

Rubidium Carbonate, Rb_2CO_3.—The normal salt is obtained by decomposing the sulphate with baryta water and evaporating the filtrate with ammonium carbonate. It is a deliquescent powder which is very soluble in water. If the solution of this salt be saturated with carbon dioxide, and allowed to evaporate over sulphuric acid, glittering prisms of the acid salt, $HRbCO_3$, are obtained; these have a cooling taste, and are easily soluble in water.

Detection and Estimation of Rubidium.

184 The rubidium salts when brought into the non-luminous gas flame impart to it a tint of a rather more red shade than is produced by the potassium salts.

The flame spectrum (p. 149) exhibits two characteristic lines in the violet Rbα (4202) and Rbβ (4216). These are the most valuable as the means of recognising the rubidium salts. Two other rubidium lines, Rbδ (7950) and Rbγ (7799), are seen at the red end of the spectrum; they are both less refrangible than the red potassium lines. Besides these several other characteristic lines occur. The spectrum reaction for rubidium is so delicate that 0·002 mgrm. can be readily detected (Bunsen).

Rubidium can be estimated in the same way as potassium, either by precipitation as the platinichloride or the perchlorate.[1]

Bunsen determined the atomic weight of the metal by precipitating the pure chloride by silver nitrate. He found as a mean result the number 84·8 for the atomic weight of rubidium. Grandeau obtained a closely corresponding number by the analysis of the sulphate, the same number being also found by Godeffroy, whilst Archibald by the analysis of the bromide found the number 84·841 (H = 1); 85·485 (O = 16).[2] The value at present accepted (1913) is 85·45.

[1] See also *Gazz.*, 1903, **33**, ii. 189.
[2] *Journ. Chem. Soc.*, 1904, **85**, 776.

CÆSIUM. Cs = 132·81.

185 This metal is remarkable not only as having been the first one discovered by spectrum analysis, but also because even before Bunsen's discovery of this metal, chemists had investigated certain cæsium compounds, which, however, they had mistaken for potassium salts. Thus, in the year 1846, Plattner analysed a rare mineral found in the island of Elba, and termed Pollux,[1] with the following result:—

Silica	46·20
Alumina	16·39
Ferric oxide	0·86
Potash	16·51
Soda	10·47
Water	2·32
	92·75

Plattner, being a careful experimentalist, sought for an explanation of the fact that his analysis did not add up to 100 parts although he searched in vain for all other constituents. The explanation of the enigma was given by the discovery of cæsium, for Pisani,[2] in the year 1864, found on analysis of another sample of the same mineral that the alkali which Plattner had mistaken for potassium is in reality cæsium. His analysis gave the following numbers:—

Silica	44·03
Alumina	15·97
Ferric Oxide	0·68
Lime	0·68
Cæsia	34·07
Soda	3·88
Water	2·40
	101·71

If we now calculate the quantity of cæsium oxide corresponding to the amount of potash found by Plattner as the platinum

[1] *Poyg. Ann.*, 1846, **69**, 443. [2] *Compt. rend.*, 1865, **60**, 714.

double salt, we obtain the number 35·69; if we next subtract the weight of the chloride of cæsium thus found from the weight of the mixed chlorides of cæsium and sodium as found by Plattner, we obtain the number 1·72 as the amount of soda present. These numbers correspond satisfactorily with Pisani's results, especially when we remember that the quantity of mineral analysed by Plattner was very small. Both analyses, therefore, lead to the following formula for pollux:—

$$10SiO_2+5(Cs_2O,Na_2O,CaO)+2(Al_2O_3,Fe_2O_3)+2H_2O.$$

It has already been mentioned under rubidium that cæsium occurs generally together with this and the other alkali metals. Cæsium alone is found in the mineral waters of Frankhausen, of Monte Latino in Tuscany, as well as in the Wheal Clifford Spring, one litre of this latter water containing 1·71 mgrms. of cæsium chloride (Yorke). It is a remarkable fact that plants do not take up any cæsium compounds from the soil, and in absence of potassium compounds, cæsium acts as a poison upon vegetable life (Lucanus). The sources from which cæsium is derived, and its separation from other metals and finally from rubidium, have already been described under the latter metal. Cæsium was obtained by Setterberg by the electrolysis of a mixture of cæsium and barium cyanides, and by Beketoff by heating cæsium hydroxide with aluminium to a bright red heat in a nickel retort. It can also be prepared by heating the carbonate[1] or hydrate[2] with magnesium, or the chloride with calcium[3] in a vacuum. The metal is of silver-white colour, takes fire when heated in the air, melts at 26·4°, boils at 670° (Ruff and Johanmsen), and has a specific gravity of 1·88 at 15°.[4] When exposed to the air it gradually melts and takes fire, and when thrown into water it remains on the surface and burns with a reddish-violet flame (Graefe and Eckardt). In the presence of mercury an amalgam is formed which is more electro-positive than rubidium amalgam, and hence metallic cæsium is the most electro-positive of the metals.

[1] Erdmann and Menke, *J. Amer. Chem. Soc.*, 1899, **21**, 259.

[2] Graefe and Eckardt, *Zeit. anorg. Chem.*, 1899, **22**, 158.

[3] Hackspill, *Compt. rend.*, 1905, **141**, 106.

[4] Setterberg, *Annalen*, 1882, **211**, 100; Eckardt and Graefe, *Zeit. anorg. Chem.*, 1900, **23**, 378. See also Menke, *J. Amer. Chem. Soc.*, 1899, **21**, 420.

COMPOUNDS OF CÆSIUM.

186 The cæsium compounds are isomorphous with those of potassium, rubidium, and ammonium (p. 218). They colour the flame of a still more reddish tint than the salts of rubidium.

Cæsium Monoxide, Cs_2O, may be obtained by exposing cæsium to an insufficient amount of oxygen in a silver boat, exhausting the apparatus and distilling off the excess of metal.[1] It forms orange-red crystals, which become darker when heated and melt at 450—500° and then lose cæsium, forming a higher oxide. It absorbs water and carbon dioxide from the air, and is rendered incandescent by the addition of water, a colourless solution of the hydroxide being produced.

Cæsium Hydroxide, CsOH, is obtained by a process similar to that by which rubidium hydroxide is prepared, and resembles it closely; it is the strongest of all bases.

Peroxides of Cæsium.—When molten cæsium is exposed to oxygen and the mass heated to 300—350°, the *peroxide*, CsO_2, is formed as a yellow crystalline powder, which readily dissociates when further heated and is decomposed by water with formation of cæsium hydroxide and hydrogen peroxide, and evolution of oxygen. This oxide is also formed by the action of oxygen on cæsium dissolved in liquid ammonia, the oxides Cs_2O_2 and Cs_2O_3 being obtained as intermediate products.[2]

Cæsium Chloride, CsCl, crystallises in small cubes of sp. gr. 3·972, which melt at a dull red heat, and volatilise even more readily than potassium chloride. It is very hygroscopic and deliquesces in moist air; 100 parts of water dissolve 174·7 parts of the salt at 10°. The *bromide*, sp. gr. 4·38, and *iodide* are similar to the corresponding potassium salts. Like the rubidium halides, the cæsium derivatives form a very large number of well-crystallised double salts with other metallic halides. A number of polyhalide salts are also known, most of which are crystalline; among these may be mentioned $CsBr_3$, $CsBr_5$, CsI_3, CsI_5, and $CsCl_4I$ (Wells, Penfield and Wheeler). The polyiodide CsI_9 exists at 25°, but has not been isolated (Abegg).

[1] Rengade, *Compt. rend.*, 1906, **143**, 592.

[2] Rengade, *Compt. rend.*, 1905, **140**, 1183; 1906, **142**, 1149; *Zeit. anorg. Chem.*, 1906, **50**, 67.

Cæsium Sulphides.—Cæsium forms the same series of sulphides as rubidium, and their preparation is similar. The *pentasulphide* melts at 202°.

Normal Cæsium Sulphate, Cs_2SO_4, forms short, hard, prismatic crystals of sp. gr. 4·24, insoluble in alcohol, though readily soluble in water. The *acid salt*, $CsHSO_4$, crystallises in rhombic prisms.

Cæsium Selenate, Cs_2SeO_4, has the sp. gr. 4·4528; 100 parts of water dissolve 244·8 parts of the salt at 12°.[1]

Cæsium Nitrate, $CsNO_3$, crystallises in small glittering prisms which possess the cooling taste of saltpetre, and are slightly soluble in alcohol. 100 parts of water at 3·2° dissolve 10·58 parts of this salt. It has the sp. gr. 3·687, and melts at 414°.

Normal Cæsium Carbonate, Cs_2CO_3.—This salt separates out from a syrupy solution in the form of ill-defined hydrated deliquescent crystals. They melt on heating, leaving a residue of the anhydrous salt as a sandy powder. It is soluble in absolute alcohol. 100 parts of alcohol dissolve at 19°, 11·1, and at the boiling point, 20·1 parts of the anhydrous salt. The *acid salt*, $CsHCO_3$, crystallises from aqueous solution in large prisms.

Cæsium Hydride,[2] CsH, and *Cæsium Amide*,[3] $CsNH_2$, closely resemble the corresponding potassium compounds.

Detection and Estimation of Cæsium.

The spectrum of cæsium contains, in addition to the two characteristic bright blue lines Csα and Csβ (4555 and 4593), several other less distinct lines.

The atomic weight of cæsium has been ascertained by the analysis of the halogen salts by means of silver nitrate. Johnson and Allen as well as Bunsen thus obtained the number 132·0, whilst Godeffroy obtained the number 131·6.

Richards and Archibald[4] by the analysis of the chloride and bromide, and by heating the nitrate with silica have obtained the value 131·874 (H=1), 132·879 (O=16). The material employed was purified by recrystallisation of the dichloroiodide, $CsCl_2I$. The value at present accepted (1913) is 132·81.

[1] Tutton, *Journ. Chem. Soc.*, 1897, **71**, 846.
[2] Moissan, *Compt. rend.*, 1903, **136**, 587.
[3] Rengade, *Compt. rend.*, 1905, **140**, 1536.
[4] *Zeit. anorg. Chem.*, 1903, **34**, 353.

AMMONIUM COMPOUNDS.

187 The name *volatile alkali* was long ago given to ammonia as pointing out its similarity to the fixed alkalis potash and soda. In 1808, Seebeck made the interesting discovery that when mercury is brought into a strong aqueous solution of ammonia, and an electric current passed through it, the metal increases rapidly in bulk, giving rise to an amalgam-like mass. The same observation was made almost simultaneously by Berzelius and Pontin, whilst Davy, as soon as he was informed of the fact, repeated the experiment and discovered that a piece of sal-ammoniac moistened with water might be employed instead of aqueous ammonia. Davy also noticed that the same amalgam-like mass is formed when an amalgam of potassium is thrown into a concentrated solution of sal-ammoniac. Hence he, like Berzelius, came to the conclusion that ammonia must contain oxygen, and that in this experiment it, like potash and soda, had been reduced by the electricity to a metal-like body. To this metal-like substance, which was supposed to exist in this amalgam, they gave the name of *ammonium*. This view of the constitution of the ammonium compounds was objected to by Gay-Lussac and Thénard, who, from their experiments on the subject carried out in the year 1809, concluded that the formation of the amalgam is due to a combination of the ammonia with hydrogen. They arrived at this result from observing that the amalgam undergoes rapid spontaneous decomposition into mercury, ammonia, and hydrogen gas. Arguing from analogy, the French philosophers were inclined to believe that in like manner potassium and sodium could not be considered to be true metals, but were rather the hydrogen compounds of the alkalis. In reply to these objections, Davy and Berzelius showed that the hydrogen which was evolved might arise from the decomposing action of the metallic ammonium upon the water which adhered to it, in the same way as hydrogen is evolved when sodium and potassium are thrown into water. Berzelius continued for many years to hold the view that oxygen is contained in ammonia, and he explained the fact that this element could not be detected in the ammonia, by assuming that nitrogen itself is an oxide of an element hitherto not isolated, to which he gave the name of *nitricum*.

Ampère was the first, in the year 1816, to endeavour to explain

the analogy of the ammoniacal salts with those of the fixed alkalis. He showed that the differences in composition between the salts of a fixed and those of the volatile alkali disappear when we assume that, in the latter class of salts, a compound radical exists composed of one volume of nitrogen to four volumes of hydrogen, so that sal-ammoniac or hydrochloride of ammonia may be regarded as the chloride of the metal-like substance to which the name of ammonium had been given. In 1820 Berzelius gave up his old view, and accepted the ammonium theory. He showed that aqueous ammonia must be regarded as a solution of ammonium oxide, and assumed that when anhydrous ammonia unites with a hydrogen acid (a substance to which we now give the simple name of acid) the ammonia combines with the hydrogen of the acid to form the metal-like radical ammonium, and that this becomes an oxide by union with the oxygen of the water.

According to our present views, the ammonium salts are considered as being derived from acids by the replacement of their hydrogen by the radical ammonium, NH_4. These salts are isomorphous with the salts of potassium, rubidium, and cæsium, and otherwise exhibit a close analogy with them (p. 218).

Ammonium Amalgam.—This substance, whose existence has already been mentioned, is formed when a piece of moistened sal-ammoniac is laid in a platinum basin, a small quantity of mercury poured upon it, and this brought in contact with the negative pole of an electric battery, the positive pole being connected with the platinum basin. It may be obtained, still more readily, by throwing sodium amalgam containing 1 per cent. of sodium into a concentrated solution of sal-ammoniac. The mercury increases in bulk to upwards of twenty times its original volume, and then contains from 0·6 to 0·9 per cent. of its weight of ammonium. It is also produced by the action of sodium amalgam on ammonium chloride dissolved in liquid ammonia at $-35°$.[1] This amalgam forms, at the ordinary temperature, a light, soft, buttery mass which at $-80°$ becomes a very hard metallic mass, and begins to liquefy at $-40°$, and decomposes, even at $-29°$, with evolution of two volumes of ammonia and one volume of hydrogen.

The nature of this remarkable substance has been the subject of much discussion. Some chemists have supposed

[1] Moissan, *Compt. rend.*, 1901, **133**, 803.

that it must be regarded merely as a solution of ammonia and hydrogen in mercury, or as a metallic froth. Against this view, however, it is to be remembered that neither of these gases, either alone or when mixed together, dissolves at all in mercury. Others again support the view that ammonium amalgam is a true amalgam containing the metallic radical ammonium. Ammonium amalgam differs, however, from the amalgams of the alkali metals, inasmuch as it does not reduce the salts of silver and copper at the ordinary temperature,[1] and this fact was for long considered to be strong evidence against this opinion. It has, however, been found that at 0° this reduction readily occurs, and that the amalgam is even capable of reducing the salts of cadmium and zinc.[2] The view that ammonium amalgam is in reality analogous to the amalgams of sodium and potassium is confirmed by the fact that the depression of the freezing point of mercury produced by the presence of the ammonium is similar to that produced by sodium or potassium.[3] Moreover the effect of the amalgam on the magnitude of polarisation of a battery is quite comparable with that of the amalgams of the alkali metals.[4]

When ammonium amalgam decomposes, it appears to give off positively charged ions, the nature of which is unknown.[5]

All efforts to isolate the radical ammonium, either from the amalgam or from the salts, have hitherto failed. It does not appear to be produced by the electrolysis of ammonium iodide in liquid ammonia at $-95°$[6]; nor is it formed in various reactions, such as the interaction of calcium with ammonium chloride at a low temperature in presence of liquid ammonia.[7] In all these cases ammonia and hydrogen are the products, and hence it is probable that "ammonium," if it be capable at all of an independent existence, can exist only at very low temperatures.

Potassammonium and Sodammonium.—When metallic potassium or sodium is added to liquid ammonia, solution takes place, and when the blue liquid is allowed to evaporate a copper-

[1] Landolt, *Annalen*, 1868, Suppl., **6**, 342.
[2] Coehn, *Zeit. anorg. Chem.*, 1900, **25**, 430.
[3] Rich and Travers, *Journ. Chem. Soc.*, 1906, **89**, 872.
[4] Le Blanc, *Zeit. Physikal. Chem.*, 1890, **5**, 467.
[5] Coehn, *Chem. Centr.*, 1906, ii., 409; *Zeit. Elektrochem.*, 1906, **12**, 609.
[6] Ruff, *Ber.*, 1901, **34**, 2604.
[7] Moissan, *Compt. rend.*, 1901, **133**, 715, 771.

coloured mass remains which has the composition NH_3K or NH_3Na.

Similar substances are formed by lithium, rubidium, cæsium, calcium, strontium, and barium.[1] They are also formed when ammonia is passed over these metals, and for each metal there is a limit of temperature above which the change does not occur. It has hitherto been supposed that these substances are compounds of ammonia with the metals in question, but the experiments of Ruff and Geisel [2] show that in all probability the change consists simply in the formation of a solution of the metal in ammonia, the copper-coloured residue being composed of the solid metal and its saturated solution, which can be separated by filtration through a cloth under pressure.

All the solutions of the metals in ammonia gradually decompose, forming the amide of the metal and free hydrogen, the change being much accelerated by the addition of platinised asbestos.

The metals in this form are extremely reactive, and these solutions have been employed in the preparation of many metallic compounds.

Ammonium Peroxide.—A crystalline compound of the composition $(NH_4)_2O_2,H_2O_2$ is formed when ethereal solutions of ammonia and hydrogen peroxide are mixed and cooled to $-40°$. It decomposes slowly at this temperature into ammonia and hydrogen peroxide, but at the ordinary temperature yields ammonia, water, and oxygen, a small amount of ammonium nitrite being also formed.[3]

Ammonium and the Halogens.

188 *Ammonium Fluoride*, NH_4F, is obtained by saturating hydrofluoric acid with ammonia. The commercial hydrofluoric acid, however, generally contains lead and other metals which must be previously removed by the addition of a small quantity of ammonium carbonate and sulphide. The clear acid liquid is saturated with solid ammonium carbonate and then evaporated in a platinum basin, ammonium carbonate being added at intervals to prevent the formation of the acid fluoride. Am-

[1] Joannis, *Ann. Chim. Phys.*, 1906 (8), **7**, 5; Roederer, *Compt. rend.*, 1905, **140**, 1252; Moissan, *Compt. rend.*, 1892, **127**, 685: 1901, **133**, 715; 1903, **136**, 1177.

[2] *Ber.*, 1906, **39**, 828.

[3] Melikoff and Pissarjewsky, *Ber.*, 1897, **30**, 3144; 1898, **31**, 152, 446.

monium fluoride crystallises in hexagonal tablets or prisms. It has a sharp saline taste and deliquesces in moist air, is more easily soluble in water than sal-ammoniac, and decomposes at the ordinary temperature when in the moist state. It decomposes silicates on being heated with them, with evolution of silicon tetrafluoride, and hence it is largely used in mineral analysis and for etching upon glass. This may be readily accomplished by allowing a solution of the salt to dry upon the place which it is desired to etch. It cannot be preserved in glass bottles, but must be kept in vessels either of platinum, silver, or gutta-percha.

Hydrogen Ammonium Fluoride, NH_4F,HF, is formed when a solution of the normal salt is evaporated at a temperature of about 40°. It crystallises in colourless rhombic prisms which deliquesce slightly in the air and on heating evolve highly irritating and acrid fumes.

Ammonium Chloride, NH_4Cl.—The history of this salt, well known under the name of sal-ammoniac, has already been given in Vol. I., p. 493. It is found in the fumeroles of Vesuvius, Etna, Hecla, and other volcanoes, as well as in the cracks and fissures in recent lava streams. Its formation has also been observed when large masses of coal undergo combustion, as when a coal pit is on fire. The salt has also been observed in guano from the Chincha Islands.

Sal-ammoniac originally served as the source from which all the ammoniacal salts were prepared. At present, however, these are usually obtained from ammonium sulphate, which is prepared from the ammoniacal liquor of the gasworks on an enormous scale. For the manufacture of the chloride, gas liquor is sometimes distilled with lime in the manner described under ammonium sulphate, and the ammonia evolved absorbed in hydrochloric acid of sp. gr. 1·1 contained in a stone saturator. More usually now, a crude fairly concentrated *liquor ammoniae* is first prepared by the distillation of gas-liquor, as described in Vol. I., p. 500, and then neutralised with hydrochloric acid, or a solution of ammonium sulphate is boiled with the equivalent quantity of sodium chloride, when double decomposition takes place :

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4.$$

The sodium sulphate separates first on concentration and is removed by "fishing." The solution of ammonium chloride

obtained by any of these methods is then evaporated to the crystallisation point, and the crude product purified by recrystallisation or more frequently by sublimation. The vessel employed for this purpose consists of two parts. The lower one is either a semicircular earthenware vessel embedded in an iron one, or consists entirely of a cast-iron basin. The sal-ammoniac in the solid state is brought into this, and then a semicircular dome-like cover, either of earthenware, lead, or iron, is placed over it, and this is luted tight with clay. In the centre of the dome there is an opening which is left open during the sublimation. Pure sal-ammoniac is also obtained by employing the same apparatus, but, instead of the impure salt, a mixture of common salt, NaCl, and ammonium sulphate, $(NH_4)_2SO_4$, is heated, when sodium sulphate remains behind, sal-ammoniac subliming as before.

Pure ammonium chloride is colourless and odourless and has a sharp saline taste. It crystallises from a saturated solution in arborescent or feather-like growths which consist of an aggregation of small regular octahedra, and other forms of the regular system (class 29, p. 201), so that the crystals appear to belong to the hexagonal or tetragonal system (Fig. 99). From a solution containing urea, sal-ammoniac crystallises in cubes. When the salt is sublimed, and the vapour quickly cooled, it is precipitated in the form of a light crystalline powder known as flowers of sal-ammoniac. The common sublimed sal-ammoniac is a semi-transparent, fibrous, crystalline mass, which is so tough that it is difficult to powder. For the purpose of obtaining it in a fine powder, a concentrated solution is evaporated down and constantly stirred.

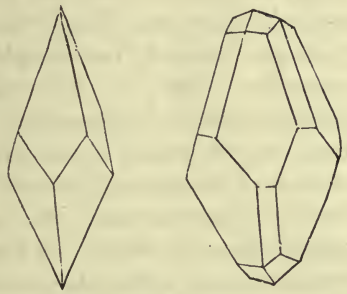


Fig. 99.

When sal-ammoniac dissolves in water a considerable reduction of temperature takes place; 30 parts of salt dissolve in 300 parts of water at 13·3°, and the temperature is reduced to −5·1° (Rüdorff). 100 parts of water dissolve at 0°, 29·7, at 10°, 33·3, and at 110°, 83·8 parts of the salt; the boiling point of the saturated solution is 115·6°.

Sal-ammoniac is very sparingly soluble in absolute alcohol, of

which 100 parts dissolve 0·62 part of the salt at 19°. The specific gravity of sal-ammoniac is 1·52.

The salt is slightly hydrolysed in aqueous solution,[1] and when the solution is boiled, ammonia escapes in small quantity, the liquid, which is at first neutral to litmus, becoming slightly acid. It is not volatile at the ordinary temperature of the air, but at higher temperatures it evaporates completely, giving rise to a colourless vapour, which, according to Bineau, has the specific gravity 0·89, corresponding to a vapour density of 13·345, whilst the molecular formula, NH_4Cl, requires a density of 26·69. From the fact of the abnormal density it has been argued that the sal-ammoniac vapour consists of a mixture of equal molecules of ammonia and hydrochloric acid. The truth of this supposition was first experimentally demonstrated by Pebal,[2] who allowed the vapour of sal-ammoniac to diffuse into an atmosphere of hydrogen, when the lighter ammonia was found to diffuse out and the heavier hydrochloric acid to remain behind. Karl von Than[3] then showed that if ammonia and hydrogen chloride be brought together at a temperature of upwards of 350°, at which point sal-ammoniac is gaseous, no change either of temperature or of the volume of the gases is observed, whereas if chemical union had taken place a change of both of these would naturally have been expected. Marignac[4] further observed that in the volatilisation of sal-ammoniac nearly the same amount of heat is absorbed as is evolved when ammonia and hydrochloric acid combine. It has also been shown that under diminished pressure and in an atmosphere of ammonia, the vapour density of ammonium chloride is 24·2—24·6, showing that under these conditions nearly the whole of the ammonium chloride volatilises without dissociation,[5] whilst if the ammonium chloride employed be absolutely dry it has the normal vapour density even under atmospheric pressure.[6]

This fact of the dissociation of sal-ammoniac can be readily shown by igniting a small piece of the solid in a closed platinum crucible. On removing the lid after the salt has been volatilised, and plunging a moistened piece of blue litmus paper into the crucible, the litmus paper will be turned bright

[1] Veley, *Journ. Chem. Soc.*, 1905, **87**, 26.
[2] *Annalen*, 1862, **123**, 199.
[3] *Annalen*, 1864, **131**, 129.
[4] *Compt. rend.*, 1869, **68**, 877.
[5] Neuberg, *Ber.*, 1891, **24**, 2543.
[6] Baker, *Journ. Chem. Soc.*, 1894, **65**, 615.

red, proving the presence of free hydrochloric acid, the lighter ammonia having escaped.

Sal-ammoniac is used in medicine. In former days that which came from Egypt was especially esteemed as a drug. Large quantities are used in the processes of dyeing, and workers in metal employ it in the processes of soldering and tinning, as at a high temperature it either reduces the metallic oxide or converts it into fusible chloride and thus gives rise to a bright metallic surface. It is also of value in the laboratory, both as a reagent and as a convenient source of ammonia.

Ammonium Bromide, NH_4Br, is very soluble in water, and crystallises in white cubes which taste like sal-ammoniac.

Ammonium Iodide, NH_4I, is best obtained by saturating ammonia with hydriodic acid. It crystallises in colourless cubes readily soluble in water and in alcohol. It deliquesces in moist air and gradually assumes a yellow colour due to the slow liberation of iodine.

A *dibromoiodide*, NH_4Br_2I, analogous in composition to the rubidium trihalogen compounds, has been described.[1]

Ammonium Chlorate, NH_4ClO_3.—When ammonia is saturated with chloric acid and the solution evaporated, this salt crystallises out in small needles, which have a strongly acrid taste and are very soluble in water and slightly soluble in absolute alcohol. Heated to 102° the salt decomposes (Wächter), chlorine, oxygen, nitrous oxide and aqueous vapour being evolved, and sal-ammoniac remaining behind. Occasionally the salt undergoes spontaneous decomposition. When thrown on to a hot plate it decrepitates like ammonium nitrate.

Ammonium Perchlorate, NH_4ClO_4, is obtained by saturating ammonia with perchloric acid. It forms rhombic crystals, which are isomorphous with potassium perchlorate and dissolve in five parts of cold water.

It has been employed as a constituent of explosives, for which purpose it may be prepared by the interaction of concentrated solutions of ammonium nitrate and sodium perchlorate.[2]

Ammonium and Sulphur.

189 The method of preparing volatile compounds of sulphur has long been known. Thus, for instance, the writer who assumed

[1] Jackson and Derby, *Amer. Chem. J.*, 1900, **24**, 15.

[2] Alvisi, *Gazz.*, 1899, **29**, i., 121, 478.

the name of Basil Valentine states that a blood-red oil may be obtained by distilling together common sulphur, quicklime, and sal-ammoniac. He also says: "Take grey sulphur and quicklime a pound, sal-ammoniac a fourth part; rub these together, when a splendid red oil is obtained, which fixes and refines." Beguin was also acquainted with this mode of preparation in the seventeenth century, and this salt was known as *spiritus sulphuris volatilis Beguinii.* Boyle in 1663 observed that the vapours of this body possessed the power of blackening metals, and he therefore termed it a volatile tincture of sulphur, and this same substance was known to the later chemists as *spiritus fumans Boylei.* This is a mixture of several sulphides of ammonium. Boerhaave in 1732 was the first to mention the fact that flowers of sulphur dissolve in ammonia, the substance thus obtained being known as volatile liver of sulphur. The preparation of the compound by leading sulphuretted hydrogen into ammonia was described by Kirwan in 1786.

Ammonium Sulphide, $(NH_4)_2S$, is obtained in colourless micaceous crystals by passing a mixture of sulphuretted hydrogen with a slight excess of ammonia into a vessel cooled to $-18°$, ammonium hydrosulphide being also formed. At the same time a very volatile liquid is condensed, which has the composition $(NH_4)_2S,2NH_3$. Ammonium sulphide readily dissolves in water, but the properties of the solution render it probable that it is at the same time partially dissociated into ammonium hydrosulphide and ammonia.[1]

Ammonium Hydrosulphide, NH_4HS, is obtained by mixing sulphuretted hydrogen and ammonia in equal volumes at the ordinary temperature, and forms a porcelain-like mass; it is also formed if the sulphuretted hydrogen be present in slight excess, but is not the only product in presence of excess of ammonia. Its aqueous solution is obtained by saturating ordinary strong ammonia solution, diluted with four times its volume of water, with sulphuretted hydrogen, the strongest solution obtainable containing 16–19 per cent. of NH_4HS. If the solution of ammonia be more concentrated, compounds of the general formula $(NH_4)_2S,xNH_4HS$ are formed, the value of x decreasing step by step with the increase in the concentration of the solution. Thus with ammonia of specific gravity 0·880 the compound formed has the composition $(NH_4)_2S,2NH_4HS$, and separates, when the solution is cooled to 0°, in leaf-like

[1] Bloxam, *Journ. Chem. Soc.*, 1895, **67**, 283.

crystals. Crystals having the composition $(NH_4)_2S,6NH_4HS$, $(NH_4)_2S,12NH_4HS$, and $(NH_4)_2S,18NH_4HS$ have also been prepared. The ammonium sulphide solution employed in the laboratory consists, therefore, of ammonium sulphide, hydrosulphide, hydroxide, and free ammonia in proportions varying with the concentration, and it also almost always contains a small quantity of polysulphides, which impart to it a yellow colour, these being formed by the action of the solution on the sulphur obtained from its partial oxidation.

Ammonium Polysulphides.—Compounds containing more sulphur than the foregoing are obtained by the action of sulphur on solutions of ammonium sulphide; these were first examined by Fritsche, who described the tetrasulphide, $(NH_4)_2S_4$, the pentasulphide, $(NH_4)_2S_5$, and the heptasulphide, $(NH_4)_2S_7$, and regarded these as formed by the direct addition of sulphur to ammonium sulphide. The subject has been again investigated by Bloxam,[1] who has found that the formation of these compounds does not proceed in so simple a manner. The solution of ammonium sulphide, which as above mentioned usually contains the hydrosulphide, sulphide, and free ammonia, acts on the sulphur with evolution of sulphuretted hydrogen and formation of two tetrammonium polysulphides viz., the *enneasulphide* $(NH_4)_4S_9$ and the *heptasulphide* $(NH_4)_4S_7$, both of which crystallise in yellow needles, and contain respectively seven and four molecules of water. These compounds by their decomposition give rise to the diammonium polysulphides, of which the following have been obtained in the crystalline form:

Ammonium tetrasulphide, $4(NH_4)_2S_4, H_2O$.
Ammonium pentasulphide, $(NH_4)_2S_5, H_2O$.
Ammonium heptasulphide, $3(NH_4)_2S_7,4H_2O$.
Ammonium enneasulphide, $2(NH_4)_2S_9,H_2O$, and $5(NH_4)_2S_9,4H_2O$.

190 *Normal Ammonium Sulphate*, $(NH_4)_2SO_4$.—We find this salt mentioned by Libavius, but more accurately described by Glauber, who recommended its use as a medicine. It was long known by the name of *sal ammoniacum secretum Glauberi.* This salt is found in certain volcanic districts, especially in the neighbourhood of the boric acid fumeroles of Tuscany, and it is termed by mineralogists mascagnite. Ammonium sulphate is prepared on the large scale by heating ammoniacal gas liquor with milk

[1] *Journ. Chem. Soc.*, 1895, **67**, 283.

of lime, and passing the ammonia evolved into sulphuric acid. The distillation is best carried out in a continuous still, the construction of which is analogous to the well-known Coffey still, used in the distillation of alcohol. A typical form of still, devised by Feldmann,[1] is shown in Fig. 100. The ammoniacal liquor passes from the storage tank *a* into the supply tank *b*, and thence through the economiser J, where it is warmed by the hot waste gases coming from the saturator E. It flows

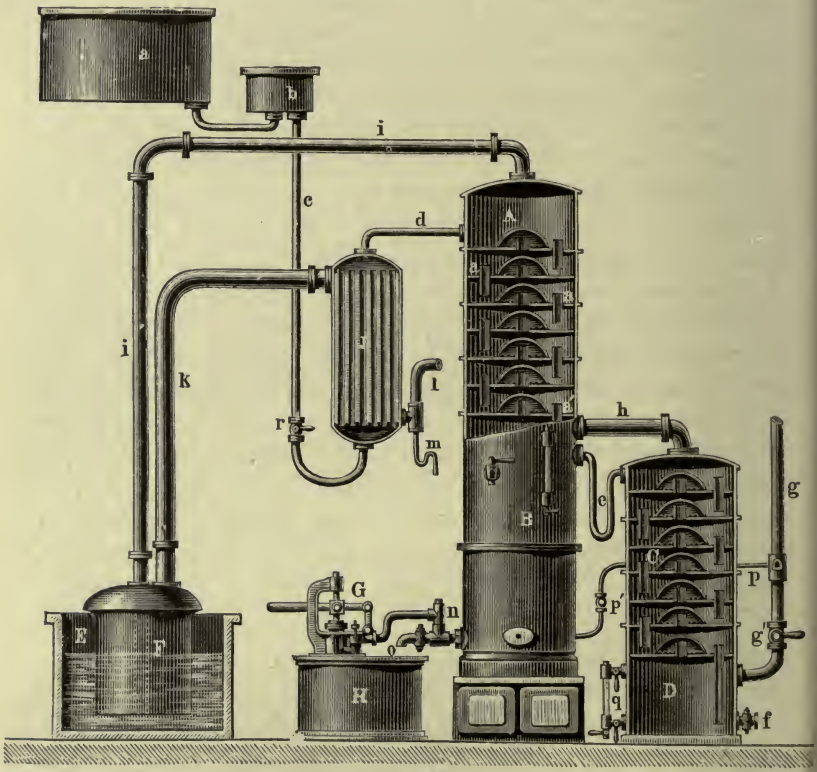


Fig. 100.

thence into the top chamber of the column A, falls from chamber to chamber by the overflow pipes *a*, and is subjected in each to a current of steam subdivided into a number of small streams, which completely removes the whole of the volatile ammonia, *i.e.*, the ammonia present as sulphide and carbonate. In the chamber B it is mixed with milk of lime introduced by the pump G, and then passes into the top of the second column C,

[1] Patent No. 3643 (1882).

where it is again subjected to the action of the current of steam and freed from the fixed ammonia, *i.e.*, that present as sulphate, chloride, thiosulphate, thiocyanate, &c., the acids remaining in combination with the lime. The waste liquor passes away from the bottom D, and is almost completely free from ammonia.

The steam required is introduced by the pipe *g* into the bottom of the column C, passes from the top to the bottom of A, and leaves the latter, carrying with it the whole of the ammonia, sulphuretted hydrogen, and carbon dioxide, by the pipe *i*, through which it is conveyed to the saturator E, which consists of an iron or wooden tank lined with lead and filled with sulphuric acid of 142° Tw. The latter absorbs the ammonia, forming ammonium sulphate, which is fished out as it separates and allowed to drain, the waste gases being retained within the bell F, and passing thence through the economiser J, to the pipe *l*, by which they are conveyed to plant for further treatment and prevention of nuisance arising from them.

These gases consist chiefly of sulphuretted hydrogen and carbon dioxide, with some hydrocyanic acid, hydrocarbon vapours, and small amounts of other impurities, and they are usually treated for the recovery of the sulphur. In some cases they are burnt with the requisite quantity of oxygen in a Claus kiln (p. 302), and the sulphur recovered as such, but in most cases the sulphuretted hydrogen is removed by absorption with oxide of iron, as in the purification of coal-gas (Vol. I., p. 871). Other methods of treatment are to burn the gas completely and pass the products of combustion with those from pyrites burners into sulphuric acid chambers, or, where no chambers are available, into a tower containing limestone, down which water flows, the sulphur being thus converted into a solution of calcium sulphite.

The ammonium sulphate thus obtained is always slightly damp and contains a small quantity of free acid, but may be purified by recrystallisation. It forms large transparent crystals isomorphous with those of potassium sulphate, has a specific gravity of 1·77, and a sharp, bitter, and saline taste. 100 parts of water dissolve at 0°, 71 parts, and at 100°, 103·3 parts of the salt, but it is only slightly soluble in aqueous alcohol and insoluble in absolute alcohol.

Ammonium sulphate can be obtained by heating aluminium nitride with sulphuric acid or with aluminium sulphate:

$$2AlN + H_2SO_4 + 6H_2O = 2Al(OH)_3 + (NH_4)_2SO_4.$$

It is suggested to use the product so obtained as fertiliser.[1]

Ammonium sulphate is used for the manufacture of other ammonium salts, but its chief employment is as a nitrogenous manure, this salt and Chili saltpetre being the two chief sources of inorganic nitrogenous matter employed in agriculture. It is estimated that in 1912 the world's consumption of these salts for manurial purposes was no fewer than 2,555,200 tons of Chili saltpetre, and about 1,300,000 tons of ammonium sulphate.[2] The whole of the ammonia of commerce, as already mentioned, is obtained as a by-product in the distillation of coal, by far the greatest quantity being obtained from the coal-gas manufacture. Increasing quantities of ammonia are, however, being recovered in other industries where coal is distilled, namely, from coke-ovens, blast-furnaces, shale-works, bone-works, and in the manufacture of producer gas from bituminous fuel (Vol. I., p. 892). The following table gives the amount of ammonium sulphate produced in the United Kingdom in the years 1909-10-11[3]:—

	1911.	1910.	1909.	
Gas-works . . .	168,789	167,820	164,276	tons
Iron-works . . .	20,121	20,139	20,228	„
Shale-works . .	60,785	59,113	57,048	„
Coke-oven works .	105,343	92,665	82,886	„
Producer-gas and carbonising works (bone and coal) . .	20,964	27,850	24,705	„
Total . .	376,002	367,587	349,143	tons

In 1912 the production of ammonia calculated as sulphate was estimated at 379,000 tons made up as follows:[4]

Gas-works	166,000	tons
Iron-works	20,000	„
Shale-works	61,000	„
Coke and carbonising works and producer-gas works .	132,000	„
Total	379,000	tons

[1] German Patent, 235868.

[2] Compare Guye, *J. Soc. Chem. Ind.*, 1906, **25**, 568.

[3] Chief Inspector's Forty-Eighth Annual Report, 1911, p. 17.

[4] *Chemical Trades Journal*, 1913, **52**, 82.

Ammonium Persulphate, $(NH_4)_2S_2O_8$.—This salt is obtained by the electrolysis of a solution of ammonium sulphate in dilute sulphuric acid, and crystallises in large prisms, which are very soluble in water.[1] In presence of silver salts it undergoes a remarkable decomposition, one-eighth of the nitrogen being oxidised to nitric acid:[2]

$$8(NH_4)_2S_2O_8 + 6H_2O = 7(NH_4)_2SO_4 + 9H_2SO_4 + 2HNO_3.$$

It is now prepared on the manufacturing scale for use as an oxidising agent, also for the preparation of other persulphates, as it is the most soluble of all these salts.

Ammonium Selenate, $(NH_4)_2SeO_4$, is not isomorphous with the rhombic sulphate, but forms monoclinic crystals. In the presence of a small amount of sulphate, however, mixed crystals of the rhombic system are obtained.[3]

Ammonium and Nitrogen.

191 *Ammonium Azoimide* or *Ammonium Nitride*, N_4H_4 or $NH_4.N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$, is formed by neutralising a solution of azoimide with ammonia, but is best obtained by saturating an alcoholic solution of diazohippuramide, $C_9H_8NO_2.NH.N{:}N.OH$, with ammonia gas; it crystallises in large lustrous prisms, which become opaque and slowly volatilise in the air, and on careful heating sublime in small lustrous prisms. It is very soluble in water, has an alkaline reaction, melts and decomposes violently at 110°, and explodes with great violence when quickly heated.[4] When it is vaporised the salt dissociates completely.[5]

Ammonium Nitrite, NH_4NO_2, is best obtained by passing the nitrous fumes prepared by the action of nitric acid on arsenious oxide over ammonium carbonate kept cool by ice, the resulting mass being treated with alcohol, and precipitated with ether. It forms colourless deliquescent crystals which explode on heating to 60–70°, whilst in acid solution similar decompositions sometimes occur at the ordinary temperature.[6] It can also be prepared

[1] Marshall, *Journ. Chem. Soc.*, 1891, **59**, 777.

[2] Marshall, *Proc. Roy. Soc. Edin.*, 1900, **23**, 163; Marshall and Inglis, *ibid.*, 1902, **24**, 88.

[3] Tutton, *Journ. Chem. Soc.*, 1906, **89**, 1059.

[4] Curtius, *Ber.*, 1891, **24**, 3348.

[5] Curtius and Rissom, *J. pr. Chem.*, 1898 (2), **58**, 261.

[6] Sörensen, *Zeit. anorg. Chem.*, 1894, **7**, 33.

from ammonium sulphate and sodium nitrite.[1] The solution decomposes on heating with formation of nitrogen and water (Vol. I., p. 493):

$$NH_4NO_2 = N_2 + 2H_2O.$$

Ammonium Nitrate, NH_4NO_3.—This salt was first prepared by Glauber and was originally known by the name of *nitrum flammans*. It has a specific gravity of 1·72, and melts at 166°, It is tetramorphous, forming a cubic modification which is stable above 125·6°, a hexagonal modification stable from 125·6° to 82·8°, a rhombic form stable from 82·8° to 32·4°, and finally a second rhombic form stable below this temperature,[2] which is the form obtained by the evaporation of the solution at the ordinary temperature. It is very soluble in water, a large amount of heat being absorbed ; 100 parts of water dissolve 118·3 parts of the salt at 0°, 241·8 parts at 30°, and 580 parts at 80°. The cryohydric temperature is –17·35° (de Coppet). It is also easily soluble in alcohol and dissolves in liquid ammonia. When the dry salt is thrown on a red-hot plate it decomposes with the production of a yellow flame and a slight explosion, into nitrogen, water, and nitric oxide, whereas if it be gently heated it decomposes into water and nitrous oxide, a small portion of the salt subliming unchanged. It is chiefly employed in the manufacture of nitrous oxide for anæsthetic purposes, and is also used for the preparation of freezing mixtures, and as a constituent of certain explosives. The salts $NH_4NO_3,2HNO_3$, melting at 29·5°, and NH_4NO_3,HNO_3 have been described.[3]

Ammonium and Phosphorus.

192 *Normal Ammonium Phosphate*, $(NH_4)_3PO_4$, is obtained as a crystalline semi-solid mass when hydrogen di-ammonium phosphate is supersaturated with concentrated aqueous ammonia. It crystallises from its solution in dilute ammonia in short prismatic needles. These contain $3H_2O$, and are moderately stable in the air, but on boiling the aqueous solution two-thirds of the ammonia is evolved.

[1] Biltz and Gahl, *Zeit. Elektrochem.*, 1905, **11**, 409.

[2] Lehmann, *Zeit. Kryst. Min.*, 1877, **1**, 106 ; Schwarz, *Preisschrift, Göttingen*, 1892, 42 ; Tammann, *Ann. Phys. Chem.*, 1899 (2), **68**, 553, 629 ; Müller and Kaufmann, *Zeit. physikal. Chem.*, 1903, **42**, 497 ; Nicol, *Zeit. anorg. Chem.*, 1897, **15**, 397. Compare Wallerant, *Compt. rend.*, 1906, **142**, 217.

[3] Groschuff, *Ber.*, 1904, **37**, 1486 ; *Zeit. anorg. Chem.*, 1904, **40**, 1.

Di-ammonium Hydrogen Phosphate, $(NH_4)_2HPO_4$, occurs in guano from Ichaboe (Herapath), and is easily formed when a solution of phosphoric acid containing an excess of ammonia is allowed to evaporate; transparent monoclinic prisms are thus deposited.

Ammonium Dihydrogen Phosphate, $(NH_4)H_2PO_4$, is formed when aqueous phosphoric acid is added to ammonia until the solution reddens litmus paper, and is no longer precipitated by barium chloride. It crystallises in tetragonal prisms and is isomorphous with the corresponding potassium salt.

Hydrogen Ammonium Sodium Phosphate or *Microcosmic Salt* $HNaNH_4PO_4,4H_2O$.—The old alchemists were aware that this peculiar salt could be obtained from urine, but Marggraf was the first to examine with care the salt which crystallised from evaporated urine and to show that it contained a volatile alkali, whilst Proust found in 1775 that sodium was contained in this compound. The salt was first termed *sal urinæ fixum* in contradistinction to the *sal urinæ volatile* or ammonium carbonate, but it was also termed *sal microcosmicum*, being obtained from the human body. This compound is also found in guano (Herapath).

In order to prepare the compound, five parts of common rhombic sodium phosphate are dissolved in hot water together with two parts of crystallised ammonium phosphate, and the solution is allowed to cool. Transparent monoclinic prismatic crystals separate out, having a specific gravity of 1·55 and possessing a strongly saline taste. They melt readily on heating, giving off water and ammonia, and leaving a residue of the dihydrogen sodium orthophosphate, which again at a high temperature melts with loss of water, forming a clear liquid, and this on cooling yields a glassy mass of sodium hexametaphosphate. This substance is used largely as a blowpipe reagent.

Ammonium and Carbon.

193 *Carbonates of Ammonia.*—Commercial carbonate of ammonia, *sal-volatile*, or salt of hartshorn, forms the starting-point for these compounds. This substance was well known to the later alchemists, who prepared it by the dry distillation of evaporated and decomposed urine, hartshorn, bones, and other animal matter. Its preparation from sal-ammoniac was first described in the works attributed to Basil Valentine, but long

after the 15th century it was supposed that the volatile alkaline salts obtained from various sources possessed different medicinal power. Even up to the end of the 17th century *English drops*, which were really nothing more than carbonate of ammonia mixed with an ethereal oil, were sold at high prices, and it was stated by some that the volatile alkali contained in this substance was prepared by the destructive distillation of silk, whilst others gave the remarkable receipt that five lbs. of skulls of persons who had been hanged, or had otherwise come to an unnatural end, must be distilled with two lbs. of dried vipers, hartshorn, and ivory. More rational views concerning the composition of these compounds were arrived at towards the end of the 18th century. Dossie in his *Elaboratory laid Open*, published in 1758, distinctly states that the same animal substances alway yield an equally efficacious kind of volatile alkali.

Commercial Carbonate of Ammonia is obtained by subliming a mixture of two parts of chalk and one part of sal-ammoniac or ammonium sulphate. This operation is conducted in iron retorts furnished with leaden receivers, and ten parts of sal-ammoniac yield from seven to eight parts of the carbonate. This salt is then resublimed with the addition of some water, and is thus obtained as a white, semi-transparent, fibrous mass, which has a strongly ammoniacal smell and a pungent caustic taste. This salt possesses the composition $N_3H_{11}C_2O_5$, and consists of hydrogen ammonium carbonate along with ammonium carbamate (Vol. I., p. 854); thus, $(NH_4)HCO_3 + NH_4.CO_2NH_2$. By treating the salt with strong alcohol the carbamate can be dissolved whilst the ammonium bicarbonate remains undissolved. This same decomposition takes place when the salt is exposed to the air, the carbamate undergoing slow volatilisation.

The impurities liable to occur in the commercial salt are thiosulphate, sulphate, and chloride of ammonia, lead from the receiver, and lime and calcium chloride from the chalk employed.

Normal Ammonium Carbonate, $(NH_4)_2CO_3,H_2O$.—Dalton first prepared this salt by treating sal-volatile with a quantity of water insufficient to dissolve it completely. It is also obtained when ammonium carbamate is dissolved in water, a condition of equilibrium between the two salts being finally attained:[1]

$$CO\begin{cases}NH_2\\ONH_4\end{cases} + H_2O \rightleftharpoons CO\begin{cases}ONH_4\\ONH_4\end{cases}.$$

[1] Macleod and Haskins, *J. Biol. Chem.*, 1906, 1, 319.

It is, however, most readily prepared by digesting the common commercial carbonate of ammonia for two hours at a temperature of 12° with strong aqueous ammonia, and drying the crystalline powder which remains behind between blotting paper.

Transparent tabular or prismatic crystals are deposited from a solution prepared at a temperature of from 30° to 35°. These possess an ammoniacal odour, attract moisture from the air and become opaque from loss of ammonia and formation of hydrogen ammonium carbonate and water (Divers).[1]

Hydrogen Ammonium Carbonate or *Ammonium Bicarbonate*, $(NH_4)HCO_3$.—Crystals of this salt are sometimes found in Patagonian guano, and in the purifiers of gas-works. It is formed when the foregoing compound is allowed to lie exposed to the air, or when its solution is treated with carbon dioxide. It forms a white mealy powder, or, when slowly crystallised, large rhombic crystals, which have a cooling saline taste and do not smell of ammonia when in the dry state. At 60° it slowly undergoes decomposition with evolution of carbon dioxide, ammonia, and water. When it is more strongly heated in such a way that a small quantity of water condenses and the gases are not allowed to recombine, the ordinary commercial carbonate of ammonia is formed (Divers). This salt dissolves at 15° in 8 parts of water. Its solution when exposed to the air, as well as when heated above 36°, loses carbon dioxide, but its saturated solution can be crystallised by cooling out of contact with air. It is not soluble in alcohol, but if alcohol be added and the mixture be allowed to stand in the air carbon dioxide is evolved and normal ammonium carbonate dissolves. It forms a double salt with the former compound having the composition $2(NH_4)HCO_3,(NH_4)_2CO_3,H_2O$, which is known as ammonium sesquicarbonate; this may be most easily obtained by treating the commercial salt at 30° with a moderate amount of tolerably concentrated ammonia, and crystallising. This double salt forms flat rhombic prisms or thin six-sided tablets, smells strongly of ammonia, and dissolves at 15° in 5 parts of water. It is decomposed by an excess of water with formation of the bicarbonate. Aqueous solutions of the carbonates are completely decomposed on boiling, the ammonia and carbon dioxide passing over with the steam.

194 *Ammonium Cyanide*, NH_4CN.—When a mixture of sal-ammoniac and dry ferrocyanide of potassium, or mercury

[1] *Journ. Chem. Soc.*, 1870, **23**, 171.

cyanide, is heated, this salt sublimes in colourless cubes which smell of both ammonia and hydrocyanic acid. It is also produced when a mixture of ammonia, nitrogen and hydrogen is passed over wood charcoal at 1000°.[1] It is easily soluble in both water and alcohol, and evaporates at a temperature of 36°. The vapour is inflammable and burns with a yellow flame. It is an extremely poisonous salt, and decomposes, especially in the moist state, into azulmic acid.

Ammonium Cyanate, NH_4OCN, is formed, mixed with urea and cyamelide, when the vapour of cyanic acid is brought into contact with dry ammonia, but is obtained nearly pure by mixing ethereal solutions of ammonia and cyanic acid at 20°[2], and is formed in solution when concentrated solutions of potassium cyanate and ammonium sulphate are mixed. It forms a friable mass, easily soluble in water and sparingly soluble in absolute alcohol. This salt, as is well known, easily undergoes intramolecular change, forming the isomeric urea, $CO(NH_2)_2$ (Vol. I., p. 854).

Ammonium Thiocyanate, NH_4CNS, is formed when a solution of yellow ammonium sulphide, which contains polysulphides, is warmed with hydrocyanic acid:[3]

$$(NH_4)_2S + HCN + S = NH_4CNS + NH_4HS.$$

It is obtained on the large scale by this reaction from the hydrocyanic acid present in crude coal-gas (Vol. I., p. 875), but in the laboratory is most readily prepared by mixing together 600 grams 95 per cent. alcohol, 800 grams ammonia (specific gravity 0·912), and 350 to 400 grams carbon disulphide, and allowing to stand for several days, then distilling off a portion of the liquid, and allowing the remainder to crystallise.[4] Ammonium thiocarbonate, $(NH_4)_2CS_3$, is first formed in this reaction, but decomposes on heating into the thiocyanate and sulphuretted hydrogen:

$$(NH_4)_2CS_3 = NH_4CNS + 2H_2S.$$

It is very readily soluble in water and alcohol, crystallising out in colourless plates. Its solution in water is attended with great absorption of heat; thus if 100 grams of the salt be dis-

[1] Lance, *Compt. rend.*, 1897, **124**, 819.

[2] Walker and Wood, *Proc. Chem. Soc.*, 1898, 108; *Journ. Chem. Soc.*, 1900, **77**, 21.

[3] Liebig, *Annalen*, 1847, **61**, 126.

[4] Schultz, *J. pr. Chem.*, 1883 (2), **27**, 518.

solved in an equal weight of water at 17°, the temperature sinks to −12° (Rüdorff). The perfectly dry salt melts at 159° and when slowly melted is partially converted into the isomeric thio-urea $CS(NH_2)_2$[1] (Vol. I., p. 858).

Ammonium thiocyanate is always found amongst the products of the dry distillation of organic substances containing nitrogen and sulphur, and is therefore always present in gas liquor. Its formation is brought about partly by the combination of the hydrocyanic acid in this gas with ammonium polysulphide, partly by the interaction of the ammonia, sulphuretted hydrogen, and carbon disulphide, in the manner already explained.

HYDROXYLAMINE SALTS.

195 Hydroxylamine, NH_2OH, the preparation of which has already been described (Vol. I., p. 521), forms salts with acids which are analogous to those of ammonia; the most important of these are as follows:

Hydroxylamine Hydrochloride, NH_2OH,HCl, crystallises from a hot alcoholic solution in monoclinic prisms or plates, which are very soluble in water but less so in alcohol. When heated it decomposes into ammonium chloride, hydrochloric acid, water, and nitrogen. When a concentrated solution of this salt is treated with an alcoholic solution of hydroxylamine, it yields the salt $(NH_2OH)_2HCl$ as a crystalline precipitate, which when mixed with concentrated solutions of the normal salt yields large, well-formed crystals having the composition $(NH_2OH)_32HCl$, and melting at 95° with decomposition.

Hydroxylamine Hydriodide, NH_2OH,HI, forms flat, colourless, very hygroscopic needles,[2] which are obtained by evaporating the solution in vacuo below 26°. The compounds $(NH_3O)_3HI$ and $(NH_3O)_2HI$ are also known.[3]

Hydroxylamine Sulphate, $(NH_2OH)_2,H_2SO_4$, crystallises from aqueous solution in large monoclinic prisms, according to Lang, or triclinic prisms according to Dathe, and is precipitated in needles on addition of alcohol to the aqueous solution.

Hydroxylamine Nitrate, NH_2OH,HNO_3, is obtained by decomposing a solution of the hydrochloride with silver nitrate, or of the sulphate with barium nitrate. On evaporating the solution

[1] Reynolds and Werner, *Journ. Chem. Soc.*, 1903, **83**, 1; Findlay, *ibid.*, 1904, **85**, 403.

[2] Wolffenstein and Groll, *Ber.*, 1901, **34**, 2417.

[3] Dunstan and Goulding, *Journ. Chem. Soc.*, 1896, **69**, 839.

over sulphuric acid an oily liquid remains, which, when pure, forms crystals melting at 48°, and readily remains in superfusion. It is very readily soluble in water and alcohol, and its aqueous solution decomposes on the water-bath with evolution of nitrous fumes.

HYDRAZINE SALTS.

196 Hydrazine, N_2H_4, like ammonia, readily combines with acids to form salts, which may for convenience be described here, although they do not correspond to the ammonium salts and those of the alkalis, hydrazine being a di-acid base. The monacid salts, $N_2H_5.X$, are as a rule much more stable than the di-acid salts, $N_2H_6:X_2$. The salts are for the most part obtained by neutralising hydrazine hydrate (Vol. I., p. 516) with the acid whose salt is required, and evaporating the solution to the point of crystallisation.

Hydrazine Dihydrochloride, $N_2H_4,2HCl$, crystallises in regular octahedra, which rapidly attract moisture from the air. It melts at 198°, losing hydrogen chloride and forming the *monohydrochloride*, N_2H_4,HCl, which forms long needles melting at 89°.

Hydrazine Dihydrobromide, $N_2H_4,2HBr$, and *Hydrazine Hydrobromide*, N_2H_4,HBr, are very similar to the hydrochlorides, and melt at 195° and 80° respectively.

Hydrazine Dihydriodide, $N_2H_4,2HI$, can only be obtained by the action of fuming hydriodic acid on benzalazine, $C_6H_5.CH:N.N:CH.C_6H_5$, and is a very hygroscopic substance which melts at 220°, and becomes brown in the light. The *monohydriodide*, N_2H_4,HI, is formed by the action of iodine on an alkaline solution of hydrazine hydrate:

$$5N_2H_4,H_2O + 2I_2 = 4N_2H_4,HI + 5H_2O + N_2.$$

It forms long colourless prisms, melts at 127°, and explodes violently at a higher temperature.

Trihydrazine Dihydriodide, $3N_2H_4,2HI$.—This salt is prepared by the addition of iodine to a solution of hydrazine hydrate in a little alcohol till crystals separate in quantity. It crystallises in large white needles melting at 90°.

Hydrazine Nitrate, N_2H_4,HNO_3, crystallises in long prisms, melts at 69°, and explodes when quickly heated. The *di-acid*

salt is very unstable,[1] and decomposes when heated, yielding azoimide, ammonium nitrate, nitrogen, nitric acid, and water.

Hydrazine Sulphate, N_2H_4,H_2SO_4.—The method of preparation of this salt has been already mentioned in describing the preparation of hydrazine (Vol. I., p. 514). It crystallises in thick lustrous tablets or long thin prisms, belonging to the rhombic system, and is sparingly soluble in cold but readily soluble in hot water, and insoluble in alcohol. It melts at 254°, and simultaneously undergoes decomposition, yielding hydrazine sulphite, sulphur dioxide, sulphuretted hydrogen, and sulphur.

Hydrazine Nitride or *Hydrazine Azoimide*, N_5H_5 or $N_2H_4,HN\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right.$, is obtained by the action of hydrazine hydrate on ammonium azoimide, or azoimide itself, and forms large vitreous prisms, melting at 65°, which deliquesce in the air, and gradually volatilise. It is sparingly soluble in alcohol, from which it crystallises in lustrous plates, and explodes with great violence when quickly heated or touched with a white-hot wire.[2] It burns like gun-cotton when a light is applied to it.

[1] Sabanieff, *Zeit. anorg. Chem.*, 1899, **20**, 21.
[2] Curtius, *Ber.*, 1891, **24**, 3348.

THE COPPER GROUP.

Copper, Cu. Silver, Ag. Gold, Au.

197 The metals of this sub-group, as has already been pointed out, differ very considerably from the other metals of the same group. Like the alkali metals, they form a series of characteristic salts in which each atom of the metal replaces one of hydrogen, but, except in the case of silver, other series of salts are known which are more stable than the first-named series. As is frequently the case with metals having very high atomic weights, gold differs in many respects from the elements of the same sub-group which have a lower atomic weight, and also shows considerable resemblance to the elements having nearly the same atomic weight; thus gold resembles platinum and iridium in many respects, and is sometimes classed with these metals.

COPPER. Cu = 63·57

198 Copper of all the metals is the one which was first employed by man. This is explained by the fact that copper occurs in the native condition, and thus requires no metallurgical treatment. In the Hebrew Scriptures copper is termed *Nehósheth*, a word derived from the root *nahásh*, to glisten. This is translated by Χαλκός in the Septuagint, and this again by *Aes* in the Vulgate. By both of the latter words the ancients understood, not only copper, but brass and bronze. Copper was afterwards specially designated as *aes cyprium*, or simply *cyprium*, a name which afterwards became *cuprum*.

The Latin Geber appears to have noticed that copper is easily attacked by acid liquids, and hence it was termed *meretrix metallorum* by the alchemists. Inasmuch as it was obtained from Cyprus, copper was considered to be the metal specially sacred to Venus, and in the writings of the alchemists it is generally known by the name of this goddess and symbolised by ♀. In the works attributed to Basil Valentine we find noted the power possessed by iron to precipitate metallic copper from solutions of its salts. In his *Last Testament* we read: "The cement or *ley* from Schmölnitz in Hungary eats iron into slime, and when the iron mud is taken out of the trough it is found to be good ♀ (copper)." In his *Currus Triumphalis Antimonii* he says, "From iron a ♀ (copper) can be got by natural means, as, for instance, by an acrid ley from Hungary which gives to it (the iron) such a metallic colour that it is converted into the best copper."

It would thus appear that this change was regarded as a transmutation of iron into copper, and Paracelsus and many other chemists seem to have held similar views with respect to this reaction. Wedel in 1664 made special inquiry into the nature of the wonderful transmutation of iron into copper by means of this Hungarian liquor; and so late as 1690 Stisser, who was professor of chemistry in Helmstedt, believed that the formation of copper precipitate was a proof of the possibility of the transmutation of metals.

It was long before these erroneous views concerning this precipitation of copper were corrected, although Van Helmont rightly surmised that the copper existed in the solution from which it was precipitated by the iron. Boyle first proved this to be the case, and in his *History of Fluidity and Firmness*,[1] published in the year 1661, he describes the precipitation of copper from its solutions by metallic zinc, and in 1675 in his *Treatise on the Mechanical Causes of Chemical Precipitation*,[2] explains the action of iron upon copper solutions by the supposition that the solvent permits the metal to be precipitated in order to take up the precipitant.

Copper occurs in the native state in various parts of the world, especially in the copper region of Lake Superior, where, sometimes in enormous masses, it occurs in veins traversing red sandstone and trap. It is also found in the same condition in Cornwall, the Faroe Islands, Siberia, and the

[1] *Op.* 1, p. 377. [2] *Op.* 4, p. 329.

Urals, and in many localities in North and South America. Native copper almost invariably contains small quantities of silver and a few other metals, such as bismuth, lead, &c. Cupric oxide, CuO, black oxide of copper, also occurs in nature, as tenorite or melaconite, and cuprous oxide, Cu_2O, occurs in larger quantities, as cuprite or red copper ore. Many copper salts occur native; of these the most important are malachite, $CuCO_3.Cu(OH)_2$; azurite or blue carbonate of copper, $2CuCO_3,Cu(OH)_2$. Copper also occurs widely distributed in combination with sulphur as vitreous copper, chalcocite, or copper glance, Cu_2S; covellite or indigo copper, CuS; copper pyrites, or chalcopyrite, $CuFeS_2$, and erubescite or purple copper ore, Cu_3FeS_3.

Copper is found in the animal kingdom in the blood of certain crustacea and arthropoda as a faintly-blue compound called *hæmocyanin*, which has similar oxygen-carrying properties to hæmoglobin, the compound of iron contained in the blood of vertebrates, whilst the livers of some of the cephalopods also contain copper.[1] This element also forms about 7 per cent. of the red pigment turacin which occurs in the feathers of birds of certain species.[2]

It has also been detected in small quantities in plants grown in ordinary soils,[3] and in larger quantities when the plants have been grown in soils containing copper.

199 *Copper Smelting.*—The methods in use for the extraction of copper differ considerably, according to the nature of the ore from which the metal is to be obtained. Both dry and wet processes of extraction are employed, the greater quantity of the metal being obtained by the former.

Two different classes of dry processes are successfully at work; (1) smelting in reverberatory furnaces, and (2) smelting in blast furnaces. The first class comprises the *Welsh* or *English process*, formerly carried out in the Swansea district of South Wales, but now modified in many directions, and also the modern method of smelting in reverberatory furnaces carried out in many important districts.

In the old *Welsh process*, a mixture of copper ores was usually employed, consisting of copper pyrites and copper carbonates, mixed with iron pyrites containing silicates and gangue, mostly

[1] Henze, *Zeit. physiol. Chem.*, 1901, **33**, 417.
[2] Church, *Proc. Roy. Soc.*, 1893, **51**, 399.
[3] MacDougal, *Bot. Gaz.*, 1899, **27**, 68.

consisting of quartz. To obtain the pure metal six distinct operations were required, viz.:

(1) Calcining the mixed ore.
(2) Preparing "coarse metal."
(3) Calcining the "coarse metal."
(4) Preparing "fine metal."
(5) Roasting to obtain metallic copper.
(6) Refining.

The calcination of the crude ores was generally carried out in kilns or reverberatory furnaces.

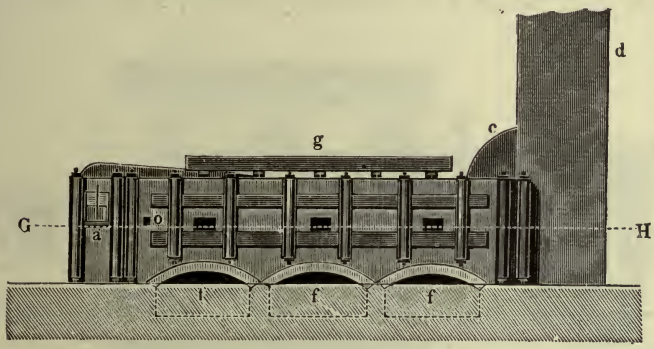


Fig. 101.

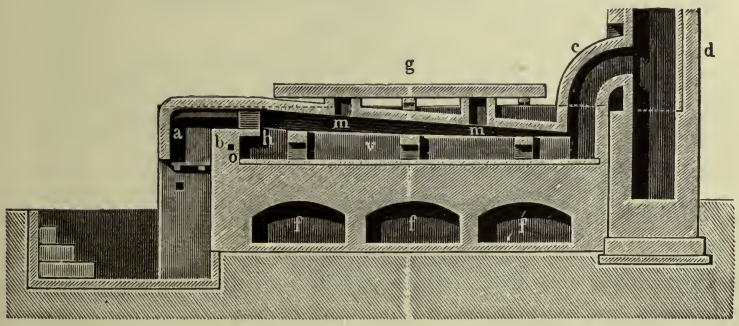


Fig. 102.

Figs. 101, 102, and 103 show the construction of the ordinary calcining furnace, into which the mixture of ore, weighing about three-and-a-half tons, was introduced from the trough *g*.

This charge was then spread evenly over the hearth of the furnace by means of long iron rakes introduced through the working doors, of which there were three on each side. The ore

was stirred from time to time to expose fresh surfaces to the oxidising action of the air, until after the lapse of from twelve to twenty-four hours, sufficient quantities of the oxides of copper and iron were formed. The roasted charge was then raked through the openings (*e e*, Fig. 103), into the arched chambers (*f f*, Fig. 102). The result of this operation was the partial oxidation of the sulphides of copper and iron, with the formation of the corresponding oxides, and the conversion of any copper carbonate present into oxide.

In the second operation the roasted ore was mixed with "metal slag" derived from the "fine metal" operation, and strongly heated in a smelting reverberatory furnace, Figs. 104 and 105,

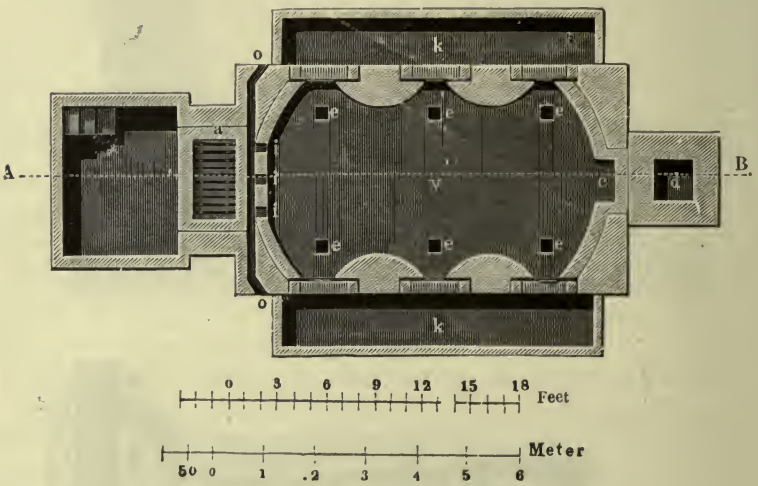


Fig. 103.

which had a much larger grate area in proportion to the size of the hearth than the calcining furnace, as it was desired to obtain a fused mass or *regulus* consisting of a mixture of the sulphides of copper and iron, termed *coarse metal*, and at the same time, a slag consisting of a silicate of iron and containing little or no copper, called *ore-furnace slag*. The temperature needed in this smelting operation is much higher than that required in the previous operation, and the chief chemical changes which go on are quite simple. The copper oxide of the roasted ore reacts with a portion of the sulphide of iron with formation of copper sulphide and oxide of iron, this latter oxide then combining with the silica present to form a fusible slag of iron silicate. In

order to obtain by this means an ore-furnace slag free from copper, it is found that the mixture of ore brought into the furnace must not contain more than 14 per cent. of copper,

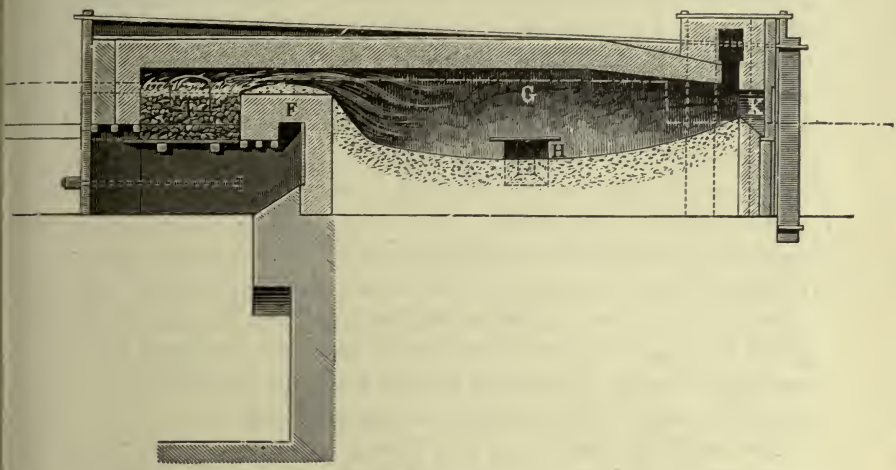


Fig. 104.

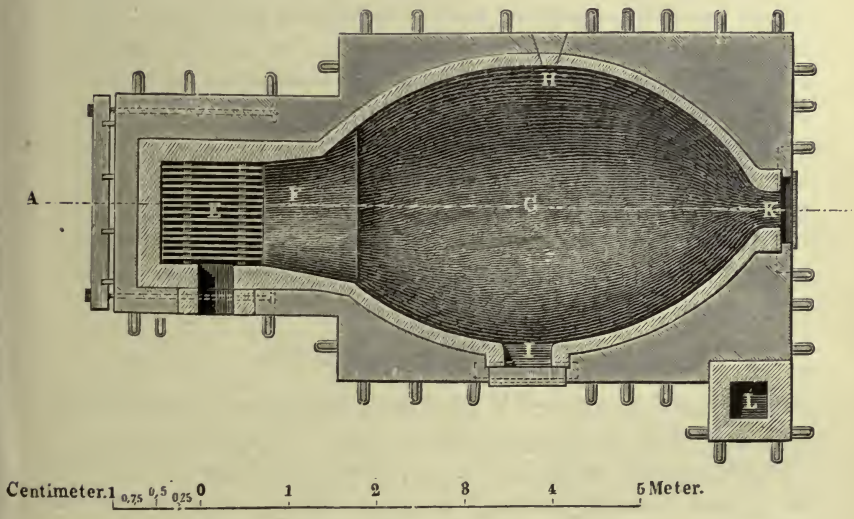


Fig. 105.

whilst, on the other hand, the percentage of copper ought not to be below 9, otherwise the consumption of fuel becomes extravagant. The coarse metal, or crude copper sulphide, usually contains about 35 per cent. of copper. The slag is

drawn off, and the fused coarse metal is run out through the tap-hole into a granulator, into sand beds or into iron moulds.

The third operation consisted of the calcination of the granulated or crushed regulus of coarse metal, for the purpose of oxidising a portion of the sulphur, leaving only sufficient to combine with the copper present, so that when again smelted, in the fourth operation, with the addition of *roaster-slag*, *refinery-slag*, and a certain proportion of oxidised ores, such as the carbonate or oxide, a nearly pure cuprous sulphide, Cu_2S, called *white metal* or *fine metal*, and containing about 75 per cent. of copper, is obtained.

If the amount of oxidised ore be insufficient, the product contains sulphide of iron and is then known from its colour as "blue metal," whilst if an excess be employed some of the copper sulphide is reduced, and sulphur dioxide evolved; the latter in its attempt to escape gives the surface a pimply appearance, the product being therefore known as "pimple-metal."

The smelting furnace used in this operation was identical in construction with that employed in the first fusion, and the slags formed chiefly consisted of iron silicate, but contained some quantity of copper, and were termed *metal slags*; these were retreated, as has been stated, in the first smelting process.

The fifth operation, consisting of the roasting of white metal to metallic copper is used to a considerable extent in present day practice and for this purpose the pigs were formerly and are now charged into a reverberatory furnace, in such a manner that air can circulate round each pig, thus subjecting them to a slow roasting process. In this way the oxide formed reacts with the unoxidised sulphide with the production of metallic copper and sulphur dioxide:

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

The metal thus reduced is filled with cavities and covered with blisters, hence it is termed *blister-copper*. It still contains from 2 to 3 per cent. of foreign matter, chiefly consisting of sulphur, iron, and other impurities. In cases where a very impure ore has to be dealt with, it has been found of great advantage to replace the ordinary silica lining of the roaster furnaces, and also of the refinery furnaces employed in the subsequent process, by a basic lining, a purer product and much less slag being obtained, arsenic especially being more readily eliminated.[1]

[1] Gilchrist, *J. Soc. Chem. Ind.*, 1891, **10**, 4.

To remove the above 2 to 3 per cent. of impurities, the blister-copper is subjected to the sixth, or refining operation, which is also used at the present time. For this purpose the blister-copper is again fused in a smelting-furnace constructed like the others, except that its floor is inclined towards a point near the door and near the chimney. Upon this floor a charge of about eight tons of blister-copper is brought, and the slags having been removed by skimming from the surface of the molten metal, this is well stirred up, or *rabbled*. The metal in this condition is termed *dry copper*. In this state it is, however, unfit for use, as it contains a proportion of oxygen, in combination as cuprous oxide, which renders it brittle. To eliminate this, the metal has to be *toughened*. This is effected by covering the surface of the molten metal with a thin layer of anthracite, and plunging a pole of wood into the molten metal. Large volumes of reducing gases consisting of hydrocarbons and carbon monoxide are thus evolved, and the metal boils up violently, the oxide being effectually reduced. After the *poled* metal has remained quiescent for a few minutes a sample is removed by the refiner, cast into a mould, and the casting cut half through with a cold chisel and broken. From the appearance and colour of the fractured surface an experienced eye can at once decide whether the copper has arrived at what is termed the *tough-pitch*, in which condition it contains just sufficient oxygen to overcome the injurious effects of the small quantities of impurities present. When this is reached, the charge must be withdrawn from the furnace as rapidly as possible and cast in iron moulds, in order to prevent a second oxidation occurring. Sometimes the molten metal becomes what is called *over-poled*, and if this is the case the metal must be exposed to the air for a short time to bring it back again to the tough-pitch.

Figs. 106 and 107 (p. 406) show the construction of a smelting furnace with a gas-generator (A) fired with coal which is filled from the shaft (C). The air necessary for the combustion of the generated gas is admitted by the openings (*b b*), whilst that required for the oxidation of the charge enters by the openings (K K).

The subject of the toughening of copper and of the removal of the non-metallic impurities contained in commercial copper is somewhat complex, and has received much attention from metallurgists. From the experiments of Abel[1] it appears that

[1] *Journ. Chem. Soc.*, 1864, **17**, 164.

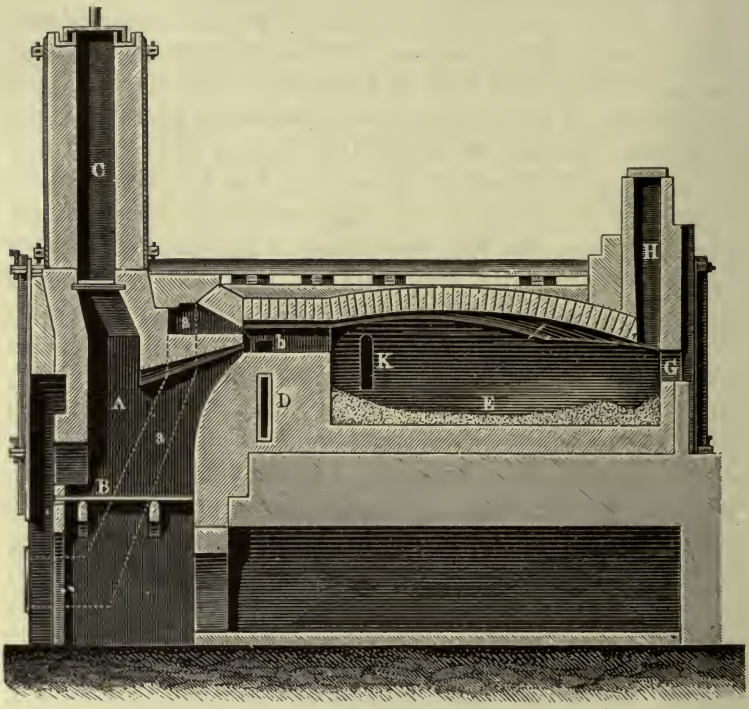


FIG. 106.

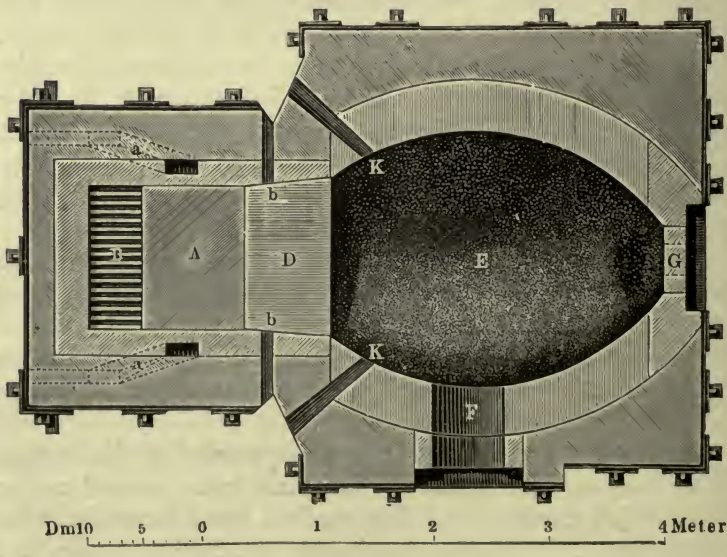


FIG. 107.

toughened copper always contains a certain amount of oxygen present as suboxide, and this agrees with the observation of copper smelters, who find that the whole charge may become over-poled in a few seconds, this being explained by the fact that the whole of the oxygen has been withdrawn. According to Hampe,[1] on the other hand, the phenomenon of the over-poling of copper depends partly on the absorption of carbon monoxide and hydrocarbons, and especially on the reduction of small quantities of lead oxide and bismuth oxide, which the copper contains, so that if these bodies be not present no over-poling occurs.

This method of copper smelting is seldom used exactly as described, but is improved by the use of one or more of the following modifications.

Large mechanical furnaces are often used for the calcination of the ore and coarse metal, in place of the old-fashioned calcining furnace. In some cases revolving cylinders, similar in principle to the Oxland calciner employed in roasting tin ores (see Tin), and in other cases, long-bedded reverberatory furnaces fitted with mechanical rabbles, such as the O'Hara, are used. A large number of other mechanically worked calciners have also been designed and worked with success, such as the Pearce Turret furnace, the Brown Horseshoe, the Merton, the Edwards, the MacDougal, and others.

In some cases also it is the practice to use shaft-furnaces or small blast furnaces for the second operation, that is for the smelting of the roasted ores for the production of "coarse metal." This effects a considerable economy in labour and fuel. In some cases also shaft-furnaces are used for the fourth operation, the production of "white metal."

The use of gas-fired reverberatory furnaces for the refining operation, having regenerators for heating the gas and air necessary has also been introduced.

In modern smelting, *reverberatory furnaces* are used for matte-smelting of finely-divided ores such as concentrates. Before charging, the ore is partially roasted, generally in one of the types of mechanical roasters, and during the smelting, the remaining sulphur unites with copper and iron forming the matte, and the silica of the gangue unites with the oxide of iron, lime, and alumina, forming a fusible slag.[2]

[1] *Chem. Centr.*, 1875, 378.

[2] Full information concerning copper smelting may be found in *The Principles of Copper Smelting*, by Peters (Hill Publishing Co., 1907), and *The Practice of Copper Smelting*, by Peters, 1911.

There has also been a considerable development in size and method of working smelting reverberatories. Furnaces capable of smelting more than 50 tons per 24 hours, with hearths measuring up to 119 feet in length, are now used as against the furnaces capable of smelting only 12 tons per 24 hours, measuring 15 feet in length, commonly used in 1880. The increase in smelting capacity is not only due to increase in size of furnace, but to certain improvements in the method of working, such as rapid charging of the hot calcined ore, preheating air by conduction through channels in the brickwork, rapid skimming through four doors simultaneously, and tapping after several charges have been smelted, thus keeping the hearth well covered with matte.

Smelting of Copper Ores in Blast Furnaces.

200 *The Mansfeld Process of Copper Smelting.*—The well-known cuprous schist or "kupferschiefer" of the Germans has been worked for copper for a long time. Agricola, writing in the middle of the sixteenth century, describes the methods adopted in his time near Mansfeld for the extraction of the metal. The first operation consists in the roasting of the schist whereby the bituminous matter is burnt off, the water and arsenic expelled, and a portion of the sulphur removed.

In the second operation the roasted ore is mixed with slag from the "black copper" operation, and smelted in blast furnaces for coarse metal and a clean slag. The coarse metal, or "rohstein," is next re-roasted and smelted for fine metal or "spurstein."

The fine metal is treated by the Ziervogel process (see Silver) for the extraction of the silver present, and the remaining copper oxide is smelted in a blast furnace for the production of black copper which is refined.

Blast furnaces are sometimes employed in the smelting of oxidised copper ores, the charge consisting of ore, necessary fluxes, and coke for fuel. The products are blister copper which is afterwards refined, and slag which invariably contains from 1·5 to 2·5 per cent. of copper.

Blast furnaces are very largely used in the smelting of sulphide copper ores, the form mostly employed being water-jacketed iron furnaces. One of the types of furnace employed is that of Herreshoff, a sectional elevation of which is shown in Fig. 108, and a sectional plan in Fig. 109. The main furnace

A, has an elliptical section and consists of a double casing of iron, A, B, C, through which water is continually circulated; the

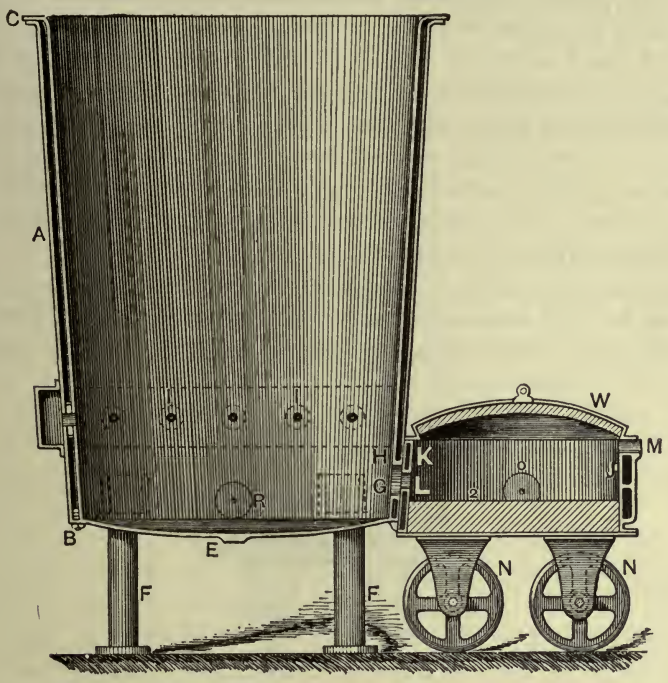


FIG. 108.

bottom of the furnace, E, is lined with fire-brick or fire-clay. The roasted ore, mixed with coke or anthracite, and the slag

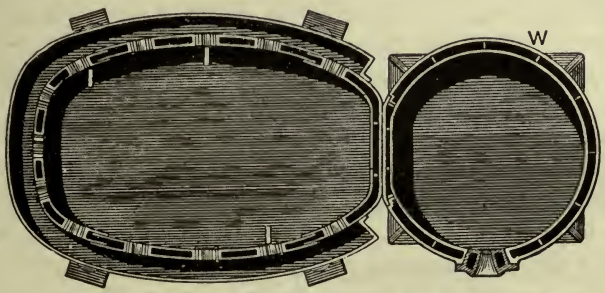


FIG. 109.

from a later process, which consists chiefly of iron silicate with a little copper, is introduced at the top of the furnace, the air

being forced through the tuyeres I I. The products, which consist of "matte" (corresponding to the "coarse metal" of the Welsh process) and slag, accumulate in the bottom of the furnace and then overflow continuously into the "fore-hearth," W, the end elevation of which is shown in Fig. 110; this is frequently mounted on wheels, N N, for convenience of moving. The slag then flows away almost continuously from the opening M, the matte being run off by the tap-hole O, as occasion requires. This matte is usually reduced to metallic copper in a "converter," the resulting metal being refined in reverberatory furnaces or by the electrolytic method.

These water-jacketed blast furnaces, generally rectangular in form, are not only more easily constructed than the ordinary brick furnaces, but can be much more rapidly heated and cooled,

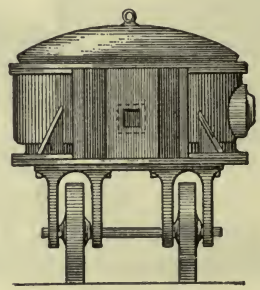


FIG. 110.

the blowing-in of the furnace and its cooling down for repairs being thus greatly facilitated. The manipulation of the furnace during the smelting is also rendered much simpler.

During recent years great developments have taken place in the sizes of water-jacketed blast furnaces used in the smelting of copper.[1] Up to the year 1885 the largest furnaces were 96 inches long by 36 inches wide, and up to 1902, the largest furnaces were 120 inches by 42 inches. In 1902 the Anaconda Copper Company built a furnace 180 inches by 56 inches, and in 1904 the same company joined up two furnaces including a space of 21 feet between, making a furnace 52 feet in length; in 1905 this furnace was joined to another 15 feet furnace, including a space of 21 feet, making a furnace 87 feet long.

Pyritic Smelting.[2]—By this is meant the smelting of sulphide ores by the heat generated by their own oxidation, without

[1] See Gowland, *Trans. Inst. Min. and Met.*, 1906–7, 265.

[2] Pyritic Smelting, *Trans. Inst. of Min. and Met.*, 1905–1906, 269.

the aid of carbonaceous fuel. In this direction great progress has been made in recent years. This process is applicable to auriferous, argentiferous, and cupriferous pyrites, and its object is to smelt for a matte in which the gold, silver, or copper will be concentrated.

In practice it is found advisable to add a small quantity, up to 5 per cent., of fuel to the charge forming a process of partial pyritic smelting. The furnaces most suitable are large, rectangular, water-jacketed blast furnaces with a larger number of tuyeres than usual for ordinary smelting.

One of the applications of this method is to smelt a mixture of pyrites, low in copper, with siliceous material carrying gold and silver; most of the sulphur and iron are oxidised, thus generating the heat, and leaving ferrous oxide which forms a slag with the silica. The unoxidised sulphur forms a matte with the copper and some iron and this matte also carries practically the whole of the precious metals. The treatment of this matte for the recovery of copper, gold, and silver is a comparatively easy matter (see Silver.)

Application of the Bessemer Process to Copper Smelting.— Mention must also be made of the reduction of metallic copper in the Bessemer converter by the Manhès process. The principle involved is the same as that of the Bessemer iron process, viz., the removal of the foreign substances by the passage of air through the molten mass, but in the manufacture of steel from 5 to 10 per cent. of the charge only has to be oxidised, whereas in treating a 25 per cent. copper matte 75 per cent. has to be disposed of.

The operations consist in charging the converter with the molten matte, blowing air to concentrate the matte up to white-metal, pouring off the slag, adding more matte to the converter, blowing to metallic copper and pouring the charge. During the blow, the sulphur and iron become oxidised, the latter combining with the siliceous lining to form a ferrous silicate slag.

The converters (Fig. 111) are similar to the steel converters, but have side tuyeres slightly elevated above the bottom and a lining often 18 inches thick. A lining generally lasts only from four to six blows, and hence this is an expensive item in converting. In some works, therefore, a siliceous ore containing 5 to 10 per cent. of copper is used as a lining, the copper being extracted during the process; thus at the Detroit copper works

200 tons of such an ore are economically smelted every month per converter.[1]

In order to obviate the necessity of constantly renewing the linings of these converters, basic linings have been introduced and are working successfully. These converters are lined with magnesite bricks, and after a small charge of matte, together with the siliceous material necessary to form a slag, has been blown, it is poured. The slag which adheres to the sides of the

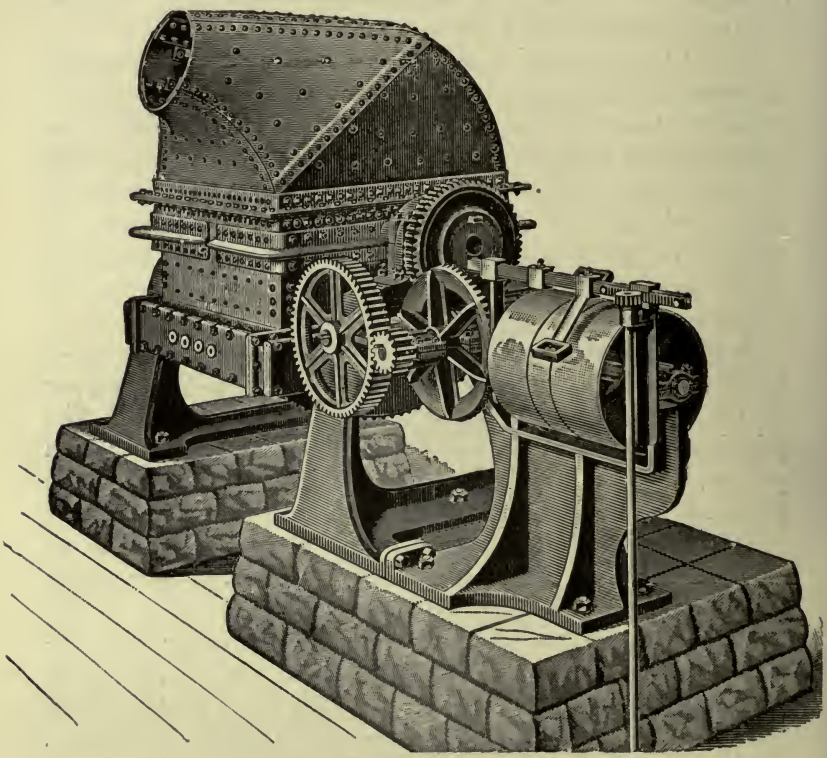


FIG. 111.

converter now forms a suitable medium for retaining a charge of siliceous material which is necessary for the reactions and which is put in the converter previously to the next charge of matte.

A converter recently installed at the smelter of the Anaconda Copper Co.[2] is 20 feet in diameter, and 17 feet high,

[1] See Treatment of Copper Mattes in the Bessemer Converter, *Trans. Inst. of Min. and Met.*, 1899-1900, **18**, 2.

[2] *Mining and Scientific Press*, 1912, 222.

and it has a lining of magnesite bricks $2\frac{1}{2}$ feet thick on the tuyere side, and 2 feet thick on the opposite side. There are 62 tuyeres each of $1\frac{3}{4}$ inches diameter and the air consumption is 25,000 cubic feet per minute. The total weight of this converter, filled with metal, is nearly 300 tons, and it is capable of producing 50 tons of copper each pour.

201 *Wet Copper Extraction Processes.*—Upwards of half a million tons of iron pyrites, containing on an average 3 per cent. of copper, are annually burnt in the sulphuric acid works of this country. The residual oxide of iron, known as burnt pyrites, or *blue billy*, is too poor in copper to render it possible to apply to it any of the ordinary dry-smelting operations. Processes for accomplishing this end have been proposed by Longmaid and Henderson, and are now carried out on a large scale, and known as the wet copper extraction processes. These

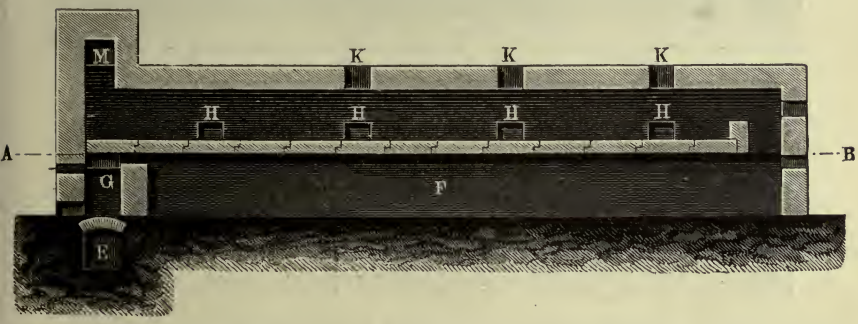


Fig. 112.

operations depend upon the fact that if the ground burnt ore be mixed with from 12 to 15 per cent. of coarsely crushed rock-salt, and the mixture properly calcined, the whole of the copper is converted into a soluble cupric chloride. The roasted mass is then lixiviated, and the copper contained in solution thrown down as metal by scrap-iron, any silver contained in the solution being previously precipitated as silver iodide by the addition of potassium or zinc iodide. The calcination is usually carried on in long furnaces shown in Figs. 112, 113, 114, and 115, the mixture of ore and salt being introduced through hoppers placed above the furnace ; the temperature is kept at a dull red heat, and the mass is frequently stirred. The ordinary furnace charge is 3 tons 5 cwts., and the operation lasts about six hours. It is found that the success of the working of the process depends upon the relative amounts of sulphur and copper

existing in the ore, the sulphur exceeding the copper by about 0·5 per cent. If the proportion of sulphur in the burnt ore be less than this, a sufficient quantity of raw pyrites must be added. During the calcination considerable quantities of chlorine and hydrochloric acid gases are evolved, together with

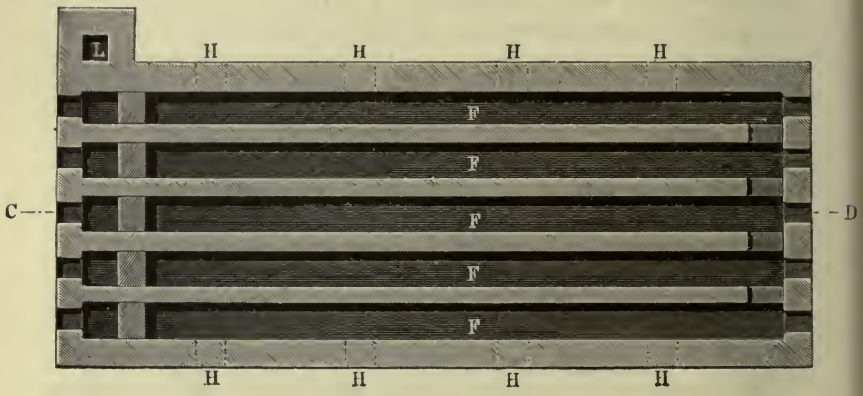


Fig. 113.

some vapours of ferric and cupric chlorides. In order to prevent these noxious vapours from passing into the atmosphere, the exit flue from the furnace is connected with a wash-tower filled with open brickwork, down which a current of water passes. The precipitate of metallic copper, thrown down from

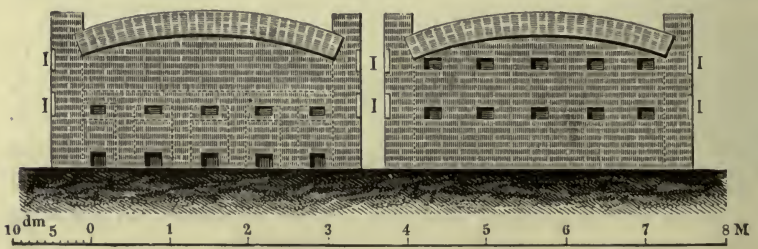


Fig. 114. Fig. 115.

the liquors by scrap-iron, contains from 70 to 80 per cent. of copper, and it is either smelted direct for blister-copper, or fused with the fine metal, Cu_2S, of the dry process, then roasted, and afterwards worked up to marketable copper by the process already described.

Another extraction process is that of Hunt and Douglas.[1]

[1] *Engineering*, 1876, 22, 419.

According to this, the ores containing carbonates or oxides are simply heated, whilst those containing sulphides must be roasted, as it is necessary for the copper to be in the form of cupric oxide.

The ore is then treated with a solution prepared by dissolving 120 parts of common salt, or 112 parts of calcium chloride, and 280 parts of ferrous sulphate in 1,000 parts of water, and then adding 200 parts of common salt. The process depends upon the fact that ferrous chloride, $FeCl_2$, is thus formed, which in contact with common salt converts the copper oxides into chlorides. If cuprous oxide be present, metallic copper is at once precipitated:

$$3Cu_2O + 2FeCl_2 = 2Cu + 4CuCl + Fe_2O_3.$$

Cupric oxide is decomposed as follows:

$$3CuO + 2FeCl_2 = 2CuCl + CuCl_2 + Fe_2O_3.$$

Cuprous chloride, although insoluble in water, is held in solution in the presence of the other chlorides, and then decomposed by iron together with the cupric chloride.

The advantage of this process lies in its requiring smaller quantities of iron for the precipitation of the copper, since part of this is present as cuprous chloride. The objections are the formation of basic salts, the difficulty of separating the solution from the residue, and the difficulty of recovering any silver present. These objections have led to the adoption of a new Hunt and Douglas process, in which the copper oxide is dissolved by means of dilute sulphuric acid, and ferrous or calcium chloride added to convert the copper into cupric chloride, sulphur dioxide being then forced through to precipitate the copper as cuprous chloride:

$$CuCl_2 + CuSO_4 + SO_2 + 2H_2O = 2CuCl + 2H_2SO_4.$$

The cuprous chloride is separated and treated with iron for the formation of metallic copper, or with milk of lime for the formation of cuprous oxide, which is smelted with carbon for the production of copper. The solution from the cuprous chloride precipitate is freed from sulphur dioxide by blowing in hot air, and is then available for dissolving a further quantity of ore. The Rio Tinto process, largely employed in Spain, consists in preparing heaps of about 100,000 tons of ore in such a manner that air circulates through the material. In this way

the copper is oxidised to sulphate, and is afterwards leached out with water and precipitated on iron.

Electrolytic Refining of Copper.

202 Copper is now refined on the large scale by means of electrolysis, this process being especially applicable in the case of impure copper containing silver or gold. For this purpose the copper is cast into slabs in which whilst still molten a copper hook is inserted to serve as a connection. The slabs are placed in a wooden tank lined with lead, and form the anodes, thin sheets of pure copper being employed as cathodes; the solution in the tank consists of $\frac{1}{2}$ lb. of sulphuric acid and 2 lbs. of crystallised copper sulphate per gallon.

For the process to work successfully it is necessary to keep the bath acid by adding sulphuric acid from time to time, and to keep up the copper content by addition of copper sulphate. It is also necessary to keep the solution in the tanks in active circulation. Nearly all the impurities, including silver, gold, platinum, tin, arsenic, antimony, and lead, are ultimately found in the precipitate or slime, which is deposited at the bottom of the tank, whilst iron, zinc, nickel, and cobalt remain in solution in the liquor.[1] This slime is usually worked up for the precious metals by charging it into a bath of molten lead on a cupel, or by treatment with sulphuric acid.

Electrotyping Process.

203 The electrolytic method is employed not only for the refining of metallic copper, but also very largely for obtaining a coating of metallic copper on any suitable object, the latter being employed as the cathode in a bath of copper sulphate solution, the anode consisting of slabs of metallic copper. This industry dates back much further than that of the electrolytic refining of copper; the latter being in reality an offspring of the electrotyping process.

In the year 1836 De la Rue, when using a Daniell's battery, observed "that the copper plate is covered with a coating of metallic copper which is continually being deposited; and so perfect is the sheet of copper thus formed, that on being stripped off it has the counterpart of every scratch of the plate on

[1] Kiliani, *Berg.- und Hütten. Ztg.*, 1885, 249.

which it is deposited." [1] This observation was followed up by other physicists, and in 1839 Jacobi of St Petersburg published his galvano-plastic process, "a method of converting any line however fine, engraved on copper, into a relief by galvanic process, applicable to copper-plate engravings, medals, stereotype plates, ornaments, and to making calico-printing blocks, and patterns for paper-hanging." [2] In the same year T. Spencer of Liverpool read a paper on the "Electrotype Process" to the Liverpool Polytechnic Society, and also in 1839 J. C. Jordan published results of experiments made with the same object.[3]

Electrotyping in copper has become a most important branch of industry, statues and other works of art being largely reproduced in this way.

For the purpose of reproducing statues, busts, and similar objects, casts of the original in gypsum or models in gutta-percha are saturated with oil, coated with graphite to give the surface the necessary conducting power, guiding wires connected to various parts of the surface, and the object then made the cathode in a bath of copper sulphate solution. When the coating is $\frac{1}{16}$th of an inch thick the process is stopped, the copper cut through in several places and the plaster core extracted. The inner surface of the various parts is then subjected to the action of sulphuretted hydrogen to coat it with a thin layer of sulphide, and these again placed in the copper sulphate bath as the cathode. As soon as the deposit on the interior is of sufficient thickness the parts are removed, the thin outer shell of copper torn off, and the parts then joined together.

For the purpose of covering iron, an alkaline solution of copper cyanide in potassium cyanide is employed. On dipping the iron or steel article into this solution a thin deposit of copper is obtained, and upon this a coating of silver or gold can easily be deposited. For the purpose of obtaining a thicker deposit of copper on iron, the operation is conducted as described and the object then placed in a copper sulphate depositing bath. The solution, according to Wilde's process, is maintained in a constant state of rotation, and the iron heated to 90° before it is placed in the warm solution of cyanide, no hydrogen then being liberated on the copper, so that the latter

[1] *Phil. Mag.*, [3], 1836, **9**, 484. [2] *Athenæum*, May 4, 1839.

[3] For a detailed account of these discoveries, see Gore's *Art of Electro-Metallurgy*.

adheres more closely to the iron. The process is now successfully applied to the economical production of coppered cast-iron rollers for calico-printing. When a new pattern is required one-half of the copper is turned off and the roller restored to its original thickness by electro-deposition at a small cost. The maintenance of the rollers to a standard size is a great advantage.

204 The following table shows the amount of copper produced in 1911, by the chief copper-producing countries:

Australasia	42,512 tons.
Canada	25,570 „
Chili	33,088 „
Germany	22,363 „
Japan	52,303 „
Mexico	61,884 „
Spain	52,880 „
United States	491,634 „
	782,234 „

205 *Alloys of Copper.*—Copper unites with a number of other metals to form alloys, many of which are of great technical importance. Among these may be mentioned brasses, alloys of copper and zinc, bronze, gun-metal and bell-metal, which are alloys of copper and tin, and German silver, which is an alloy of copper and nickel. A description of these will be found under the metal forming the second constituent of the alloy.

206 *Properties of Copper.*—Commercial copper usually contains traces of the other metals which are present in the ores, and in addition to these not infrequently arsenic, sulphur, and oxygen. Pure metallic copper is obtained either by heating the pure oxide in hydrogen, or by the electrolysis of a solution of pure copper sulphate by means of platinum electrodes.

Copper possesses a peculiar red colour, and bright metallic lustre. The true copper-red colour is, however, not seen by a single reflection, and is only observed when the light entering the eye has been many times reflected from the surface of the copper. This is well seen if a piece of straight copper foil be bent at an acute angle and held before the observer; the fine deep red copper colour is noticed near the point at which the two copper surfaces approach.

Copper is found in the native state crystallised in regular

octahedra; crystals of the same form are also found as an artificial refinery product. If a piece of phosphorus be allowed to remain for some months in contact with a clean copper wire under a solution of copper sulphate, single octahedra of metallic copper are formed together with copper phosphide (Wöhler), and a similar artificial formation of crystalline copper is observed in Golding Bird's decomposing cell,[1] as well as in the cells of Meidinger's battery. In both these cases the metal is deposited from solution very slowly.

Copper is one of the toughest of metals. It is very malleable, and may be hammered or rolled into thin leaf (Dutch metal), or drawn into fine wire. After hammering it possesses a finely fibrous silky fracture, but very slight admixture of other metals makes it more brittle, and imparts to it a less distinctly fibrous nature. Native copper has a specific gravity of 8·94; cast copper, probably because it always contains small cavities, has a specific gravity of 8·92; rolled or hammered copper 8·95; and pure electrolytic copper 8·945 (Hampe). Copper which has been distilled in a vacuum [2] has the specific gravity at 20°/4° of 8·933 and, after compression at 10,000 atmospheres, of 8·938. Very thin copper leaf transmits a greenish-blue light. When a solution of copper sulphate is allowed to remain in contact with pure zinc, pure metallic copper is deposited as a fine spongy mass, which after washing and drying forms a soft, impalpable dark-red powder.

Copper melts at 1084°·1 (Holborn and Day),[3] and in the molten state possesses a greenish-blue colour. When heated at a temperature just below that of its melting point, copper becomes so brittle that it can be pulverised in a mortar. Molten copper possesses the power of absorbing different gases, which are evolved in the form of bubbles when the metal cools, or give rise to the peculiar phenomenon known as "spitting," when a solid crust has already been formed on the surface. Spongy copper absorbs at a red-heat 0·6 times its volume of hydrogen, whilst copper wire absorbs 0·308 times its volume (Graham). Copper may be readily volatilised in an electric furnace, and condenses in the form of iridescent filaments having a red colour and a specific gravity of 8·16,[4] the vapour forming cupric oxide in contact with air.

[1] *Phil Trans.*, 1837, **127**, 37.
[2] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.
[3] *Amer. J. Sci.*, 1900, **10**, 171. [4] Moissan, *Compt. rend.*, 1905, **141**, 853.

If cupric oxide be reduced at 200° by means of hydrogen or carbonic oxide an active form of the metal is obtained which takes fire when brought into contact with bromine. The active properties are retained when the metal is kept in a vacuum, but disappear when it is submitted to hammering.[1]

Colloidal Copper.—Copper has been obtained in the form of colloidal solutions in several ways. Thus the reduction of a solution of copper chloride by stannous chloride in the presence of an alkaline tartrate yields a reddish-brown solution of copper,[2] whilst by reducing ammoniacal copper sulphate with a dilute solution of hydrazine hydrate a solution of copper is obtained which is blue by transmitted light.[3] It has also been prepared by Paal and Leuze,[4] by adding sodium hydroxide to a mixture of solutions of copper sulphate and sodium lysalbate or protalbate, products of the decomposition of albumin by sodium hydroxide, dialysing the resulting mixture and heating on the water-bath with the addition of hydrazine hydrate. If a concentrated solution of copper oxide is reduced in this manner the resulting copper solution is blue, whilst a dilute solution of the oxide yields a red copper solution.

When alcohol is added to a solution of anhydrous copper sulphate in concentrated sulphuric acid, so as to form a separate upper layer, a violet zone is first formed between the two liquids which gradually changes to brown owing to the production of a solution of colloidal copper.[5] Methyl alcohol, ether, acetone, acetic acid, and chloroform act in a similar manner.

Colloidal copper has also been obtained by passing an electric arc under water, the cathode being composed of an iron wire that has previously been dipped in copper sulphate.[6]

207 Metallic copper is largely used for a great variety of technical and domestic purposes, being especially valuable for its toughness. Next to silver, copper is the best conductor of electricity, and hence pure copper is very largely employed for

[1] Colson, *Compt. rend.*, 1899, **128**, 1458.

[2] Lottermoser, *Anorganische Colloïde* (Stuttgart, 1901), page 61.

[3] Gutbier and Hofmeier, *Zeit. anorg. Chem.*, 1905, **44**, 225.

[4] *Ber.*, 1906, **39**, 1550.

[5] A. Rassenfosse, *Bull. Acad. roy. Belg.*, 1910, 738. Consult *Grundriss der Kolloid Chemie*, Wo. Ostwald (Dresden, Steinkopff, 1911); also *Physics and Chemistry of Colloids*, by Emil Hatschek, (Churchill, 1913).

[6] Billitzer, *Ber.*, 1902, **35**, 1929.

electric light mains and submarine telegraphs. The purest copper must be employed, as very small quantities of impurities lower the conductivity to a very large extent.

COPPER AND OXYGEN.

208 These elements form six compounds as follows:—

Copper quadrantoxide, Cu_4O.
Copper trientoxide Cu_3O.
Cuprous oxide, Cu_2O.
Cupric oxide, CuO.
Copper peroxide, Cu_2O_3.
Copper dioxide or cupric peroxide, CuO_2.

Of these oxides the third and fourth have long been known, as they are formed when metallic copper is heated in the air. Copper scale, which falls from hot metallic copper when it is worked with the hammer, is a mixture of these two oxides. The portion of the scale next to the metal consists of the red cuprous oxide, while the outside portion is composed of black cupric oxide. Dioscorides and Pliny mention the existence of the red compound, indeed they distinguished two varieties, the one obtained in the form of a finely divided powder by pouring water on to the surface of freshly melted copper, and termed *flos aeris*, and the other obtained as copper scale and termed *aeris squama*. The Latin Geber explained the calcination of copper by the combustion of the sulphur which this metal was supposed to contain (Vol. I., p. 5), and many later chemists speak of copper as being more or less calxed. It was not, however, until the year 1798 that Proust distinctly stated that the black and red calces of copper were two distinct oxidation products.

They have the composition Cu_2O and CuO respectively, and give rise to characteristic series of salts, known as the *cuprous* and *cupric* salts. In addition, lower oxides of the formulæ Cu_4O and Cu_3O, and peroxides, Cu_2O_3 and CuO_2, have been prepared, none of which yield salts. Hydrated mixed oxides of the formulæ $Cu_3O_2,2H_2O$ and $Cu_4O_3,5H_2O$ have also been described by Siewert.[1]

Cuprous Oxide, Cu_2O.—This oxide occurs as cuprite or red copper ore, crystallising in octahedra and in other forms of the

[1] *Zeit. Chem.*, 1866, 363.

regular system (Class 29, p. 201) having a specific gravity of 5·75. It possesses a bright red or brownish-red colour, frequently exhibiting a diamond lustre, and also occurs in the massive state. In the mineral chalcotrichite it forms a hair-like mass consisting of small cubical crystals elongated in the direction of one of the axes.

Cuprous oxide may be artificially obtained by heating thick copper wire in a muffle for half an hour at a white heat, and then for some hours to dull redness; small dark crystals of the oxide then cover the surface of the metallic bead. It is also obtained by heating cupric oxide in a similar manner, but if too strongly heated the cuprous oxide loses a further quantity of oxygen. The finely-divided copper obtained by reducing a copper salt in hydrogen at as low a temperature as possible combines with atmospheric oxygen on exposure to the air with formation of cuprous oxide. It may be obtained in the wet way by reducing an alkaline copper solution with sugar, the oxide being deposited on warming as a bright red crystalline powder.

Cuprous oxide is also formed by the slow oxidation of the metal under water. Sage, in the year 1773, pointed out that the remains of a statue which had long lain under water were partially converted into this oxide, and J. Davy observed that an antique helmet, found in the sea near Corfu, was covered with crystals of metallic copper as well as of cuprous oxide. It has also been obtained in the crystalline state by the slow electrolytic decomposition of copper sulphate.[1]

Commercial cuprous oxide has a specific gravity of from 5·34 to 5·37, and the more finely it is divided the finer red does its colour become. It fuses at a red heat, and colours glass red. This latter property was known to the ancients, and in the middle ages many artificers understood the art of producing the red copper glass. The knowledge of this process was, however, completely lost in later times, and it was not until about the year 1827 that Bontemps in France and Engelhardt in Germany succeeded in reviving the manufacture of this ancient red glass.

Cuprous Hydroxide.—When cuprous chloride is decomposed by potash or soda, a yellow precipitate is produced, which was considered to be a partially dehydrated cuprous hydroxide, of the formula $Cu_8O_3(OH)_2$ or $4Cu_2O,H_2O$. When the method

[1] Golding Bird, *Phil. Trans.*, 1837, 127, 37.

of preparation is varied, however, the amount of water present in the dry substance also varies, and it is therefore probably not a true hydroxide.[1] The same yellow compound may be prepared electrolytically, using a platinum plate as cathode and one of copper as anode in a solution of potassium chloride.[2]

It absorbs oxygen readily and becomes of a blue colour when exposed to moist air. It dissolves in ammonia, as does red cuprous oxide, forming a colourless liquid which on exposure to the air quickly oxidises and becomes of a dark blue colour.

Cuprous oxide corresponds to the series of cuprous salts in which each atom of copper replaces only one atom of hydrogen. These are mostly white salts which are insoluble in water, and readily undergo oxidation with formation of cupric salts.

Cupric Oxide, CuO.—This substance occurs as tenorite and melaconite, as a dark earthy mass or in bright lustrous laminæ and more rarely in cubes. It can be artificially produced by the gentle ignition of the nitrate, carbonate, or hydroxide. Thus obtained it is a black hygroscopic powder which commences to decompose when heated to 1025°, cakes together and then fuses at about the melting point of copper, losing oxygen and forming Cu_2O or Cu_3O according to the temperature. If the amorphous oxide be ignited with five times its weight of caustic potash it becomes crystalline, and regular tetrahedra possessing a metallic lustre are formed (Becquerel). In copper refineries the occurrence of a crystalline oxide has also been observed. It is reduced by carbon at 700°.[3] When heated in the presence of hydrogen, carbon monoxide, marsh-gas, and other carbon compounds, it is easily reduced to the metallic state with formation of water and carbon dioxide, and hence it is largely used in the ultimate analysis of organic compounds. Cupric oxide when brought in contact with fused glass imparts to it a fine light green colour; this was known to the ancients as well as to the later alchemists, who rediscovered the fact and found that artificial emeralds could be prepared by means of copper. The writer known as Basil Valentine says, "the emerald contains sulphur veneris," and the writers of the sixteenth century who treat of the artificial production of gems all mention the fact that copper calx colours glass green."

[1] Gröger, *Zeit. anorg. Chem.*, 1902, **31**, 326.
[2] Lorenz, *ibid.*, 1896, **12**, 436.
[3] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 420.

Cupric Hydroxide, $Cu(OH)_2$, is obtained as a light blue precipitate by decomposing a solution of a cupric salt in the cold with an alkali. This precipitate, however, almost always contains a considerable quantity of alkali, and the hydroxide is obtained in a purer state by adding sal-ammoniac to the solution before precipitation, and then washing the precipitate well with warm water.

It may also be obtained by passing an electric current through a well-stirred solution of potassium nitrate, using a copper plate as anode and one of platinum as cathode.[1]

The hydroxide, after having been dried over lime, does not undergo loss of water on heating to 100°, but the freshly precipitated compound in the presence of water undergoes spontaneous dehydration, slowly in the cold, very rapidly at 100°, with formation of a black substance [2] having the composition $Cu_4O_3(OH)_2 = Cu(OH)_2 + 3CuO$. This compound when kept in a dry vacuum continues to lose water slowly, until its composition corresponds to the formula $6CuO, Cu(OH)_2$ (Sabatier). A hydrated cupric oxide of the composition $6CuO,H_2O$ has been obtained as a brown powder by the action of chlorine on cupric hydroxide suspended in a solution of potassium hydroxide.[3]

Cupric hydroxide dissolves readily in aqueous ammonia yielding a beautiful dark blue liquid, which is also produced when copper is allowed to remain in contact with aqueous ammonia, and the liquid exposed to the air. When largely diluted with water or treated with strong caustic potash, cupric hydroxide separates out from the solution, and on heating this the black hydroxide is precipitated. A solution of copper oxide in ammonia (Schweizer's reagent) possesses the property of dissolving cellulose (cotton-wool, linen, filter-paper, &c.).[4]

The above oxide and hydroxide yield the cupric salts on treatment with acids, the copper acting as a dyad. Many of the salts formed with colourless acids are colourless when anhydrous, but the hydrated salts are blue or green, the aqueous solutions having a similar colour; anhydrous cupric bromide and cupric chloride, however, are coloured. They combine with ammonia forming compounds which dissolve in water, forming deep blue

[1] Lorenz, *Zeit. anorg. Chem.*, 1896, **12**, 436.
[2] Sabatier, *Compt. rend.*, 1897, **125**, 101, 301.
[3] Mawrow, *Zeit. anorg. Chem.*, 1900, **23**, 233.
[4] Schweizer, *J. pr. Chem.*, 1857, **72**, 109.

solutions. The soluble salts have an unpleasant metallic taste and have an acid reaction to litmus.

In large doses the copper salts are poisonous, causing vomiting, but in small doses they have very little action, the cases of poisoning formerly supposed to have taken place from the presence of copper in food being probably due to the presence of organic decomposition products.[1]

Both cupric hydroxide and the black hydroxide form basic salts with other copper salts, and double basic salts with many other metals,[2] while basic salts are also known corresponding to the hydroxide $6CuO,Cu(OH)_2$ (Sabatier).

Copper Quadrantoxide, Cu_4O, is formed by careful addition of a solution of copper sulphate to a well cooled dilute solution of stannous chloride in caustic potash, the cupric hydroxide first formed being reduced by the stannous chloride with formation of the quadrantoxide and potassium stannate:[3]

$$4Cu(OH)_2 + 12KOH + 3SnCl_2 = Cu_4O + 6KCl + 3K_2SnO_3 + 10H_2O.$$

Copper quadrantoxide is an olive-green powder which undergoes no change under water if the air be completely excluded. Exposed to air it rapidly absorbs oxygen. The composition of this compound is ascertained from the action of dilute hydrochloric or sulphuric acid upon it, when the following decomposition takes place:

$$Cu_4O + 2HCl = 2CuCl + 2Cu + H_2O$$
$$Cu_4O + H_2SO_4 = CuSO_4 + 3Cu + H_2O.$$

Copper Trientoxide, Cu_3O, is prepared by heating cupric oxide at temperatures between 1,500° and 2,000°, and forms a yellowish-red mass sufficiently hard to scratch glass. It is unaffected even by concentrated mineral acids with the exception of hydrofluoric acid, but is dissolved by fused caustic potash.[4]

Copper Peroxide, Cu_2O_3, has been obtained by the anodic oxidation of copper in 12–14N caustic soda solutions with a current density greater than 0·1 ampere per sq. cm.[5] It

[1] Lehmann, *Trans. Inter. Cong. Hygiene and Demography* (London), 1891, **5**, 63.

[2] Maihle, *Compt. rend.*, 1902, **134**, 142; Recoura, *ibid.*, 1901, **132**, 1414.

[3] Rose, *Pogg. Ann.*, 1861, **120**, 1.

[4] Bailey and Hopkins, *Journ. Chem. Soc.*, 1890, **57**, 269.

[5] E. Müller and F. Spitzer, *Zeit. Electrochem.*, 1907, **13**, 25.

has been obtained also by passing chlorine into a strong solution of sodium hydroxide previously saturated with copper hydroxide.[1] This oxide is yellow, is very unstable, and possesses marked oxidising power, decomposing hydrochloric acid, forming aldehyde from alcohol, and nitrite from ammonia.

Copper Dioxide, CuO_2,H_2O, is best obtained by allowing finely divided cupric hydroxide to stand with aqueous hydrogen peroxide in the cold for several days, the mixture being frequently shaken. A crystalline precipitate is thus formed, which, after washing with water, alcohol, and ether at 0°, is dried in a vacuum. It has a yellowish-brown colour, and when moist readily decomposes above 6° ; when dry it does not undergo change at 170° but at 180° decomposes, forming cupric oxide.[2]

Cuprous Compounds.

209 *Cuprous Hydride* $(CuH)_n$.—This compound, discovered by Wurtz,[3] is deposited as a yellow or reddish-brown precipitate, when a solution of copper sulphate is treated with hypophosphorous acid or its sodium or zinc salt, at a temperature not exceeding 70°. At higher temperatures it decomposes into copper and hydrogen according to Wurtz, but according to Bartlett and Merrill[4] cupric hydride and hydrogen are really formed. It readily ignites in chlorine gas, and is decomposed by hydrochloric acid as follows :

$$CuH + HCl = CuCl + H_2.$$

Cuprous Fluoride, CuF, is best obtained by heating cuprous chloride in a current of hydrogen fluoride at 1100°–1200°, at which temperature the fluoride volatilises. It forms a ruby-red crystalline mass, or red powder, which dissolves in boiling hydrochloric acid, but, unlike cuprous chloride, is not reprecipitated by addition of water.[5]

Cuprous Chloride, CuCl.—This substance was first obtained by Boyle[6] by the action of copper on mercuric chloride. He compared the substance thus obtained, which he found

[1] E. Müller, *Zeit. anorg. Chem.*, 1907, **54**, 417.
[2] Krüss, *Ber.*, 1884, **17**, 2593. [3] *Compt. rend.*, 1844, **18**, 102.
[4] *Amer. Chem. J.*, 1895, **17**, 185.
[5] Poulene, *Compt. rend.*, 1893, **116**, 1446.
[6] *Considerations and Experiments about the Origin of Qualities and Forms*, 1664.

turned green on exposure to air, to resin or gum, and hence he gave to it the name of *resina cupri or cuprum gummatosum*. Proust obtained the same compound by the action of the dichloride on the salts of the monoxide, and J. Davy showed that cuprous chloride is formed together with the cupric salt when copper foil or copper filings are thrown into chlorine gas, when they burn with the evolution of a red light. If hydrogen chloride be passed over hot copper contained in a glass tube this compound is formed, and is seen to condense in transparent drops (Wöhler). It may readily be prepared on a large scale by a number of methods, all of which consist eventually in the reduction of cupric to cuprous chloride. For this purpose a mixture of copper and cupric oxide may be boiled with strong hydrochloric acid, or a hydrochloric acid solution of cupric chloride with copper; the metallic copper may be replaced by zinc dust or the cupric chloride by a mixture of cupric sulphate and sodium chloride, and the reduction may also be effected by sulphur dioxide. In all cases the cuprous chloride remains dissolved in the excess of hydrochloric acid, but separates out when the solution is poured into a large bulk of water, as a heavy white crystalline precipitate, which may be purified by washing. It crystallises from hot hydrochloric acid in white tetrahedra, has a sp. gr. of 3·7, and melts at about 434°, solidifying to a brown mass.

On exposure to light the moist substance quickly assumes a dirty violet tint, but if dried in absence of air and light, it only assumes a faint yellow colour on exposure. When allowed to remain in moist air it absorbs oxygen and is converted into green cupric oxychloride, $3CuO,CuCl_2,4H_2O$,[1] whilst repeated treatment with water in the presence of air converts it into cuprous oxide and cupric chloride.[2] If treated with water in an atmosphere of hydrogen or carbon dioxide, the chlorine passes completely into solution and a red residue of copper and cuprous oxide is obtained (Gröger).

Cuprous chloride readily dissolves in ammonia, forming, if air be completely excluded, a colourless solution which rapidly turns blue in the air owing to the absorption of oxygen and formation of cupric salts; this reaction has been used as a means of estimating the dissolved oxygen in water.[3]

[1] Gröger, *Zeit. anorg. Chem.*, 1901, **28**, 154.
[2] Lean and Whatmough, *Journ. Chem. Soc.*, 1898, **73**, 149.
[3] Ramsay and Homfray, *J. Soc. Chem. Ind.*, 1901, **20**, 1071.

Cuprous Chloride and Carbon Monoxide.—Cuprous chloride dissolves readily in hydrochloric acid, and this solution as well as the ammoniacal solution absorbs carbon monoxide, forming an unstable compound which separates out in nacreous scales when the concentrated solution is saturated with the gas, or when a thin paste of cuprous chloride and hydrochloric acid is saturated with carbon monoxide and water then added.[1] Under certain conditions, a crystallised compound corresponding to $2CuCl,CO,H_2O$ is obtained.[2]

Cuprous Chloride and Acetylene.—When acetylene is passed into a solution of cuprous chloride in potassium chloride acidified with hydrochloric acid a red precipitate, having the composition $(CuCl)_2,C_2H_2$, is formed. If the gas is passed into a neutral solution of cuprous chloride in potassium chloride, the precipitate produced has the composition $Cu_2H_2,(CuCl)_2,Cu_2O$ or $C_2H_2[(CuCl)_4KCl]_2$, according to the conditions of the experiment.[3]

The solution of cuprous chloride in ammonia absorbs acetylene forming a blood-red precipitate of cuprous acetylide, Cu_2C_2 or Cu_2C_2,H_2O, which is very explosive.[4] On addition of acids to this compound it is decomposed with evolution of acetylene, and has been used as a means of comparing pure acetylene (Vol. I., p. 784).

In a similar manner ammoniacal cuprous chloride absorbs other hydrocarbons of the acetylene series.

Cuprous Bromide, CuBr, is formed with ignition when bromine is brought into contact with copper heated below a red-heat. It forms a brownish crystalline mass which turns blue on exposure to sunlight, and has a specific gravity of 4·72.

Cuprous Iodide, CuI.—This is the only known iodide of copper. It is obtained by the direct combination of the two elements when heated together, or when copper is dissolved in a hot concentrated solution of hydriodic acid. If potassium iodide be added to a solution of a cupric salt, cuprous iodide is precipitated, half the iodine being liberated. The production of iodine can be prevented by the previous addition of sulphurous acid or ferrous sulphate:

$$2CuSO_4 + 2FeSO_4 + 2KI = 2CuI + Fe_2(SO_4)_2 + K_2SO_4.$$

[1] Jones, *Amer. Chem. J.*, 1899, **22**, 287.

[2] Berthelot, *Ann. Chim. Phys.*, 1901 [vii.], **23**, 32.

[3] Chavastelon, *Compt. rend.*, 1901, **132**, 1489.

[4] Keiser, *Amer. Chem. J.*, 1892, **14**, 285. See also Scheiber, *Ber.*, 1908, **41**, 3816.

A convenient way of preparing cuprous iodide is to heat copper foil, torn into shreds, in a porcelain crucible and to add iodoform in small quantities at a time. A violent reaction takes place, violet clouds of iodine are evolved, and on cooling, the copper is covered with a black scale which readily peels off, leaving a clean copper surface. This black scale consists of about 98 per cent. of cuprous iodide, and contains a little carbon and copper oxide.[1] The copper may then be reheated with iodoform until all is converted into the iodide.

Cuprous iodide is a white crystalline powder which undergoes little alteration on exposure to light, and has a specific gravity of 5·653 at 15°.[2] It melts at 628°, solidifying again to form a brown mass, which yields a green powder. It is almost insoluble in water, 1 part dissolving in 233,000 of water. When cuprous iodide is heated with cupric chloride (or bromide) it loses all its iodine and is converted into cuprous chloride (or bromide)[3]:

$$2CuI + 2CuCl_2 = 4CuCl + I_2.$$

Cuprous Sulphide, Cu_2S, occurs in nature as chalcocite, copper-glance, or vitreous copper, in rhombic six-sided tablets or prisms having a blackish lead-grey streak and a metallic lustre, which is often tarnished green or blue. It has a specific gravity of from 5·5 to 5·8. The same compound is also formed as a black brittle mass when copper is burnt in sulphur vapour, and when large quantities of copper and sulphur are fused together. Mitscherlich in this way succeeded in obtaining this compound in rhombic octahedra. It is also formed when cupric sulphide is gently heated in a current of hydrogen.

The black substance left when copper is dissolved in sulphuric acid is stated to be cuprous sulphide.[4]

Cuprous Sulphite, Cu_2SO_3,H_2O.—This salt is obtained by passing sulphur dioxide into a hot solution of cuprous acetate in acetic acid, and separates as a heavy white precipitate consisting of microscopic nacreous plates. It combines with the alkali sulphites forming a number of double salts, which are colourless crystalline compounds. The double salt $(NH_4)_2SO_3,2Cu_2SO_3$ when heated yields a bright red powder or scales of cupro-cupric sulphite, $Cu_2SO_3,CuSO_3,2H_2O$. A red modification of

[1] Lean and Whatmough, *Journ. Chem. Soc.*, 1898, **73**, 149.
[2] Spring, *Rec. trav. chim.*, 1901, **20**, 79.
[3] Barbieri, *Atti. R. Accad. Lincei*, 1907 [v.], **6**, i., 528.
[4] Adie, *Proc. Chem. Soc.*, 1899, 133.

cuprous sulphite has also been described, but it appears not unlikely that this is also a cupro-cupric salt.

Cuprous Sulphate, Cu_2SO_4, is obtained by heating powdered cuprous oxide with methyl sulphate at 160° until methyl ether ceases to be evolved:

$$(CH_3)_2SO_4 + Cu_2O = Cu_2SO_4 + (CH_3)_2O.$$

The salt is obtained as a greyish-white powder which should be washed in ether, excluding air, and dried in a vacuum. When dry, it is stable in dry air, but is immediately decomposed by water with the development of heat forming cupric sulphate and copper. It oxidises at 200°, yielding $CuO,CuSO_4$.[1]

Cuprous Nitride, Cu_3N.—Nitrogen gas does not act upon red-hot copper, but ammonia is decomposed into its elements when passed over the hot metal, the copper being rendered spongy and brittle, and losing its metallic lustre. This alteration in the metal seems to point to the formation and subsequent decomposition of a nitride which is only stable within a short range of temperature.[2] The nitride may be obtained by heating precipitated cuprous oxide in a current of ammonia gas, when a dark green powder is formed which contains 93 per cent. of cuprous nitride.[3] When potassamide is added to a solution of copper nitrate in liquid ammonia, an olive-green precipitate is produced.[4] If this precipitate be heated to 160° in a vacuum, nitrogen is evolved, and cuprous nitride remains as a black amorphous mass. The reaction is represented thus:

$$3Cu(NO_3)_2 + 6KNH_2 = Cu_3N + 6KNO_3 + 4NH_3 + N.$$

It is decomposed into its elements at about 300°, whilst acids and alkalis hydrolyse it with formation of ammonium salts or ammonia.

Nitrocopper, Cu_2NO_2, is obtained as a maroon-coloured powder by passing pure and dry nitrogen peroxide over finely divided copper (obtained by the reduction of copper oxide) at 25—30°. It decomposes into copper and nitrogen peroxide at 90°, is violently attacked by water with evolution of nitric oxide and formation of cupric nitrite and nitrate, and when placed in ammonia gas becomes incandescent, with formation of water,

[1] Recoura, *Compt. rend.*, 1909, **148**, 1105.
[2] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1245.
[3] Guntz and Bassett, *Bull. Soc. chim.*, 1906 [3], **35**, 201.
[4] E. F. Fitzgerald, *J. Amer. Chem. Soc.*, 1907, **29**, 656.

ammonium nitrate and nitrite, copper and ammoniacal copper oxide remaining behind.[1]

Copper and Phosphorus.—A number of alloys may be prepared by heating these two elements together, all of which melt at a much lower temperature than pure copper.[2] In this way also two compounds, *cuprous phosphide*, Cu_3P, and a *phosphide*, Cu_5P_2, have been obtained as hard grey crystalline masses.[3] Cuprous phosphide is also formed when phosphine is passed over heated cuprous chloride or precipitated copper at 180° to 200°, or over cold moist precipitated cuprous oxide, when it is obtained as a grey amorphous powder which oxidises in oxygen, very slowly at ordinary temperatures, rapidly and with incandescence at 100°, forming phosphorus pentoxide and copper.[4]

A black powder of the composition Cu_5P_2,H_2O is obtained when phosphine is passed into a solution of copper sulphate[5] (see also p. 438).

Cuprous Cyanide, CuCN.—When a solution of potassium cyanide is added to a solution of copper sulphate a red precipitate of cupric cyanide is first formed; when the liquid is boiled cyanogen gas is given off and a white precipitate of cuprous cyanide deposited. This same compound is formed by the action of potassium cyanide on cuprous chloride, and dissolves in an excess of the reagent. It may also be formed by heating copper acetate with aqueous ammonia in a sealed tube for two hours at 180°, when a colourless liquid is obtained containing in suspension finely divided copper and cuprous cyanide in crystalline plates.[6]

Cuprous cyanide forms a number of double compounds with other cyanides.[7]

Cuprous Thiocyanate, CuCNS.—Potassium thiocyanate gives a black precipitate of cupric thiocyanate when added to a solution of copper sulphate. This on long standing and washing is converted into white cuprous thiocyanate. If a reducing agent such as ferrous sulphate or sulphur dioxide be present

[1] Sabatier and Senderens, *Compt. rend.*, 1892, **115**, 236; 1893, **116**, 756.

[2] Abel, *Journ. Chem. Soc.*, 1865, **18**, 249.

[3] Heyn and Bauer, *Chem. Centr.*, 1906, ii., 1597; see also Granger, *Ann. Chim. Phys.*, 1898, [7], **14**, 60; *Compt. rend.*, 1903, **136**, 1397.

[4] Rubénovitch, *Compt. rend.*, 1899, **128**, 1398.

[5] *Ibid.*, **127**, 270.

[6] Vittenet, *Bull. Soc. chim.*, 1899, [3], **21**, 261.

[7] Grossmann and van der Forst, *Zeit. anorg. Chem.*, 1903, **43**, 94.

the white compound is at once precipitated. This reaction is often employed for the separation of copper from other metals in quantitative analysis, and also for the separation of thiocyanates.

Cupric Compounds.

210 *Cupric Hydride*, CuH_2.—This compound is obtained according to Bartlett and Merrill [1] by the action of heat on cuprous hydride. When freshly prepared it is a reddish-brown spongy mass, which changes after a time to a chocolate powder. It acts as a strong reducing agent, converting potassium chlorate in solution into the chloride, and the nitrate to nitrite and ammonia.

Cupric Fluoride, CuF_2.—When cupric oxide is dissolved in hydrofluoric acid and the solution evaporated, blue crystals having the composition $CuF_2,5H_2O,5HF$ separate out.[2] They are sparingly soluble in water, and are decomposed at 100° with separation of the oxyfluoride, CuF(OH). When heated with ammonium fluoride in a current of carbon dioxide, the crystals yield the anhydrous fluoride as a white amorphous powder, which becomes crystalline at 500° in an atmosphere of hydrogen fluoride.[3]

Cupric Chloride, $CuCl_2$, is formed when metallic copper is burnt in an excess of chlorine, or when the hydrated crystalline chloride is heated. The anhydrous salt may be prepared by adding a large excess of concentrated sulphuric acid very slowly to a solution of cupric chloride, care being taken that the temperature does not rise sufficiently high to decompose the chloride, when it separates out as a yellow precipitate.[4] Cupric chloride prepared from copper is a dark liver-coloured powder which on heating is converted into cuprous chloride with loss of chlorine. It readily dissolves in water, forming a green liquid; this is obtained also by dissolving the oxide or carbonate in hydrochloric acid. Greenish-blue rhombic prisms or needles having the composition $CuCl_2,2H_2O$ separate out on evaporation.

The solution saturated at 17° contains 75·6 parts of the anhydrous salt in 100 of water, and has an emerald-green

[1] *Amer. Chem. J.*, 1895, **17**, 185.
[2] Böhm, *Zeit. anorg. Chem.*, 1905, **43**, 326.
[3] Poulenc, *Compt. rend.*, 1893, **116**, 1446.
[4] Viard, *Compt. rend.*, 1902, **135**, 168.

colour, which on dilution with water changes to bluish-green. It is very deliquescent and is soluble in alcohol, the solution burning with a fine green flame and giving a characteristic channelled-space spectrum.

Basic Cupric Chloride, or *Copper Oxychloride*, $Cu_3O_2Cl_2$, $4H_2O = 2CuO, CuCl_2,4H_2O$.—This compound forms a pale blue precipitate when caustic potash is added to an excess of a solution of cupric chloride. When it is heated it loses water and is converted into a brown or blackish powder, and when moistened, this takes up three molecules of water, and changes again to a green colour.

When a solution of cupric chloride is mixed with cupric hydroxide, or when caustic potash is added to the solution of the former salt in quantity insufficient to ensure complete precipitation, a compound having the composition $Cu_4O_3Cl_2,4H_2O$ is thrown down. This substance occurs native in the form of a green sand composed of small rhombic prisms found at Atacama, as well as in Peru, Bolivia, and other places, and hence termed atacamite. According to Field, this mineral is at the present day being formed on the south coast of Chili by the action of sea-water on copper pyrites. The same compound may be artificially obtained in the crystalline state by heating common salt with an ammoniacal solution of copper sulphate to 100° (Debray), the decomposition being:

$$6NH_3+4CuSO_4+2NaCl+3H_2O=3(NH_4)_2SO_4+Cu_4O_3Cl_2+Na_2SO_4.$$

This compound is also formed when a solution of copper sulphate is boiled with a small quantity of bleaching powder solution; the product obtained occurs in commerce as a light, bright green powder, used in the arts as a pigment, and known under the name of *Brunswick green*. On heating it loses water and becomes black, but regains the green colour on moistening. Other oxychlorides of copper also are known, some being minerals and others artificial products. Cupric chloride also unites with other chlorides forming crystalline double salts.

Cupric Bromide, $CuBr_2$.—When cupric oxide is dissolved in hydrobromic acid and the solution allowed to stand in a vacuum over sulphuric acid, the anhydrous bromide separates out in dark crystals very similar to those of iodine. These are very deliquescent, and on heating in absence of air decompose into cuprous bromide and bromine.

Cupric Sulphide, CuS, occurs in nature as covellite or indigo-copper, occurring sometimes in hexagonal crystals but more frequently in the massive state as at Mansfeld, on Vesuvian lavas, and in Chili. It has a semi-metallic lustre and an indigo-blue colour, and a specific gravity of 4·6.

This compound is prepared artificially by heating cuprous sulphide with flowers of sulphur to a temperature not above that of boiling sulphur (Hittorf). It may also be prepared by triturating finely-powdered cuprous sulphide in a mortar with cold strong nitric acid until the action ceases; the powder is then washed, cupric sulphide remaining behind.[1] It may likewise be obtained as a blackish-brown precipitate by passing a current of sulphuretted hydrogen gas into a solution of a cupric salt. The finely-divided moist precipitate easily oxidises on exposure to the air. When cupric sulphide is gently heated in absence of air or in a current of hydrogen, it decomposes into sulphur and cuprous sulphide, and this method is often used for the estimation of the metal (Rose).

Several *polysulphides of copper* have been described having the formulæ Cu_2S_5,[2] Cu_2S_6, Cu_4S_5 and Cu_2S_3.[3] These are all unstable bodies, which, on keeping, slowly decompose into cupric sulphide and sulphur.

Cupric Sulphate, $CuSO_4$.—This salt, commonly termed copper sulphate, copper vitriol, or blue vitriol, has long been known, being found in solution in the drainage water of copper mines. It was for a long time confounded with green vitriol or iron sulphate, this being partially due to the fact that both frequently occur in the same drainage water, and are capable of crystallising together. In the works attributed to Basil Valentine the fact is recognised that both iron and copper vitriol can occur together, for he says: "Venus and Mars can be brought back into a virtuous vitriol." The alchemists frequently experimented on such mixed vitriols, as they believed that they contained the *materia prima* employed for the preparation of the philosopher's stone. Thus, in the above-mentioned work we read, "where copper and iron are found together gold will not be far distant."

The artificial production of copper sulphate is first described by Van Helmont in 1644, who obtained it by heating together

[1] Faraday, *Quart. Jour. Sci.*, **21**, 183.
[2] Bodroux, *Compt. rend.*, 1900, **130**, 1397.
[3] Rössing, *Zeit. anorg. Chem.*, 1900, **25**, 407.

copper and sulphur, and moistening the residue with rain-water. Glauber in 1648 proved that it might be readily obtained by boiling copper with oil of vitriol.

Copper sulphate is obtained on the large scale chiefly from copper pyrites, which is carefully roasted, the copper under suitable conditions being oxidised to copper sulphate, whilst the iron is chiefly converted into oxide. The residue is lixiviated and the copper sulphate separated from the solution by crystallisation. The mother-liquors contain both copper and iron sulphates, from which the copper may be precipitated by scrap iron. For agricultural use the presence of iron in the copper sulphate is not injurious, and for sulphate intended for this purpose the mother-liquor may be directly evaporated. The precipitated copper, as well as copper scale and metallic copper obtained by other processes or as scrap, is roasted in reverberatory furnaces, and the product is treated with dilute sulphuric acid. If the copper contains gold or silver it is treated with sulphuric acid mixed with its own volume of water, the silver and gold being left undissolved.

Where argentiferous copper ores are used, the roasted ore is added in small quantities to sulphuric acid and digested until the solution contains but little free acid. Lead and gold remain behind as an insoluble powder, and the clear liquor is run into wooden tanks lined with lead, and containing strips of copper on which the whole of the silver and part of the arsenic and antimony are deposited, whilst the greater portion of the bismuth separates as a basic sulphate. The copper sulphate solution, thus freed from other metals, is then crystallised in large lead-lined coolers, the crystals being deposited on strips of lead hung up in the liquid.

The commercial sulphate always contains small quantities of iron; this may be removed by boiling the solution with a little nitric acid, the ferrous sulphate being thus converted into ferric sulphate, which remains in the mother-liquor on recrystallisation.

Cupric sulphate is also obtained as a secondary product in the refining of silver; the silver is precipitated from a solution of the sulphate in the metallic form by strips of copper, and pure cupric sulphate remains behind.

Copper sulphate crystallises from warm saturated solutions on cooling in transparent blue triclinic crystals having the formula $CuSO_4,5H_2O$, and a specific gravity of

2·28. 100 parts of water dissolve, according to Poggiale, as follows:

At	10°	20°	30°	50°	70°	90°	100°
$CuSO_4,5H_2O$	36·95	42·31	48·81	65·83	94·60	156·44	203·32.

The salt is insoluble in absolute alcohol, and only slightly soluble in dilute spirits. When it is heated for some time to 100°, the hydrate $CuSO_4,H_2O$ remains as a bluish-white powder, which at a temperature of from 220° to 260° loses nearly all its water. Even at 360°, however, a small amount of water (0·04 per cent.) is retained; this is lost only at a temperature at which the salt begins to lose sulphur trioxide (Richards). The residue at 260° forms a white mass which is extremely hygroscopic, becoming blue on absorption of water. This reaction is sometimes used for the purpose of ascertaining the presence of water in organic liquids, and also for dehydrating the same. The anhydrous compound may be obtained in the form of grey prismatic needles by heating the hydrated sulphate with ammonium sulphate out of contact with the flame gases.[1]

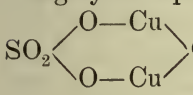
The anhydrous salt is stable up to 341°, but above this temperature, evolution of sulphur dioxide begins.[2] Between 341° and 621° small quantities of a brown oxy-salt, $8CuO,3SO_3$, are formed. Between 621° and 670° sulphur dioxide and sulphur trioxide are evolved and an orange-coloured oxy-salt, $2CuO,SO_3$, is formed. This orange-coloured salt begins to decompose at 704°, the decomposition being incomplete at 850°.

The anhydrous as well as the hydrated sulphate absorbs two molecules of hydrogen chloride with evolution of heat and formation of cupric chloride and sulphuric acid. The same decomposition takes place when copper sulphate is treated with an excess of aqueous hydrochloric acid; the temperature falls and the salts dissolve with formation of a green liquid which on concentration yields crystals of cupric chloride. This reaction of copper sulphate is employed for separating hydrochloric acid from mixtures of gases, as, for instance, from chlorine, or from carbon dioxide which has been prepared by means of hydrochloric acid. Copper sulphate is largely used in calico-printing, and in the preparation of the pigments of copper, as Scheele's green and emerald green. It is also used in very large quantity in the

[1] Klobb, *Compt. rend.*, 1892, **114**, 836.

[2] W. Uanjukoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 688.

processes of electro-metallurgy. A crude copper sulphate containing ferrous sulphate is used in agriculture for preventing "smut" in seeds.

Hydrates containing $2H_2O$ and $3H_2O$ are also known in addition to those described above, and copper also forms a series of basic sulphates. When the normal sulphate is kept for several hours at a dark-red heat, an amorphous orange-yellow powder remains behind having the composition  , which is decomposed in contact with cold water into copper sulphate and an insoluble green basic sulphate, $CuSO_4,3Cu(OH)_2$. By the action of boiling water a salt having the composition $CuSO_4,2Cu(OH)_2$ is formed. These as well as other basic salts are also obtained when a solution of copper sulphate is treated under certain conditions with potash or ammonia. Some occur as minerals; thus brochantite is a native basic sulphate having the formula $CuSO_4,3Cu(OH)_2$, and occurring in bright green rhombic tablets, whilst a basic sulphate of composition $CuSO_4,2Cu(OH)_2$ has also been found occurring in nature as a mass of small green crystals.[1] The former can be artificially prepared by allowing a piece of porous limestone to lie in a solution of copper sulphate.

When a solution of copper sulphate containing sulphuric acid is shaken with metallic copper, some cuprous sulphate is formed[2] and equilibrium is set up according to the equation:

$$CuSO_4 + Cu \rightleftharpoons Cu_2SO_4.$$

The amount of cuprous sulphate produced increases with the temperature and the concentration; thus at 100° in a solution containing originally one gram-molecule per litre of cupric sulphate, the concentration of the cuprous sulphate is 1/82 of that of the cupric salt, when equilibrium has been attained.

Cupric Nitrate, $Cu(NO_3)_2$.—In his *De furnis novis philosophicis*, published in 1648, Glauber mentions the fact that the solution of copper in nitric acid on evaporation leaves a green residue, and Boyle in 1664 observed that crystals could be obtained from the solution, and that these had the power of colouring the flame of a spirit-lamp green. In order to prepare copper nitrate, copper scale or copper oxide is dissolved in

[1] Cesaro and Buttgenbach, *Ann. Soc. Geol. Belgique*, 1897, **24**, *Bull.*, p. xli.

[2] Abel, *Zeit. anory. Chem.*, 1901, **26**, 361.

dilute nitric acid and the solution evaporated to crystallisation. In this way fine blue prismatic crystals, having the composition $Cu(NO_3)_2,3H_2O$, are obtained which melt at 114·5°, possess a caustic metallic taste, and cauterise the skin. This hydrate is stable in contact with its solution from its melting point to 24·5°, when it forms the hexahydrate, which in its turn passes at about −20° into a hydrate with $9H_2O$. The hydrated salt when heated loses nitric acid, a basic salt of the composition $Cu(NO_3)_2,3Cu(OH)_2$ being formed. Copper nitrate is deliquescent and very soluble in water, and is deposited as a fine crystalline powder when its concentrated solution is mixed with nitric acid of specific gravity 1·522. This salt, owing to the ease with which it is decomposed, possesses strong oxidising properties. If some crystals of it are wrapped up in tinfoil and rubbed, decomposition begins, often accompanied by a rise of temperature sufficient to cause emission of sparks. If a solution of copper nitrate is evaporated with one of ammonium nitrate, decomposition takes place at a certain degree of concentration attended with violent detonations. Copper nitrate is used as an oxidising agent in the processes of dyeing and calico-printing, especially in the production of catechu-browns and of some steam colours containing logwood.

Anhydrous copper nitrate[1] is prepared by the action of nitric anhydride, or a solution of this in nitric acid, on hydrated salts of copper. It is a white powder, is very deliquescent, and decomposes at 155°.

Cupric Nitrite, $Cu(NO_2)_2$, is prepared in solution by double decomposition between (*a*) cupric sulphate and barium nitrite or (*b*) between cupric chloride and silver nitrite. The solution obtained in this manner is bright grass green in colour.

According to Hampe,[2] it evolves nitric oxide even in the cold, whilst Berzelius states that it absorbs oxygen from the air and is slowly converted into nitrate.

When the solution is evaporated under diminished pressure over sulphuric acid, nitric oxide is evolved; the residue is insoluble in water, is bluish-green in colour, and consists of a mixture of nitrite and nitrate.[3]

Cupric Phosphide, Cu_3P_2, is formed when phosphine is passed over cupric chloride or when phosphorus is boiled with a cupric

[1] Guntz and Martin, *Bull. Soc. chim.*, 1909 [iv.], **5**, 1004.
[2] *Annalen*, 1863, **125**, 345.
[3] Rây, *Journ. Chem. Soc.*, 1907, **91**, 1405.

salt. It is a black powder, or, when prepared at a high temperature, a greenish-black metallic mass, which, when ignited in hydrogen, is converted into cuprous phosphide.

Normal Cupric Phosphate, $Cu_3(PO_4)_2,3H_2O$, is best obtained by dissolving the carbonate in dilute phosphoric acid and heating the solution to 70°, when a fine blue crystalline powder is deposited. On heating this with water in closed tubes it decomposes into phosphoric acid and a *basic salt*, Cu:PO_4.Cu.OH (Debray), or $Cu_3(PO_4)_2,CuO,H_2O$,[1] which latter occurs in nature as libethenite. The artificial compound crystallises in rhombic prisms, and libethenite in dark olive-green prisms, having a waxy lustre. The same compound also occurs in the massive state. Another basic copper phosphate is the mineral phosphochalcite, or pseudomalachite; this occurs in triclinic emerald-green crystals having the composition $PO_4(CuOH)_3$. Other basic phosphates of copper are known.

Copper Arsenides.—These elements combine in several proportions, whilst certain copper arsenides are found as minerals; thus whitneyite, Cu_9As, occurs as a bluish-red or greenish-white amorphous or crystalline malleable substance found in Michigan, and also in California and Arizona. Algodonite, Cu_6As, found in Chili and Lake Superior, possesses a silver-white or steel-grey lustre; and domeykite, Cu_3As, found at Portage Lake, has a tin-white to steel-grey colour. According to Reinsch, the grey deposit obtained when metallic copper is placed in a solution of arsenious oxide in hydrochloric acid has the composition Cu_5As_2, and this on heating is converted into Cu_3As. When arsenic vapour mixed with carbon dioxide or some other inert gas is passed over copper heated to the boiling point of sulphur, the arsenide Cu_5As_2 is formed, and this, when the temperature is raised, is transformed into Cu_3As.[2] The freezing point curve of copper and arsenic also points to the formation of these two arsenides.[3] When arsine is passed over dry cupric chloride the compound Cu_3As_2 is formed.

Cupric Arsenite, $CuHAsO_3$, was first obtained by Scheele by precipitating a solution of potassium arsenite with copper sulphate, and is still prepared by the same process. It is a siskin-green precipitate, which is known as a pigment under the name

[1] Caven and Hill, *J. Soc. Chem. Ind.*, 1897, **16**, 29.

[2] Granger, *Compt. rend.*, 1903, **136**, 1397.

[3] Richards, *Ber.*, 1898, **31**, 3163. See also Friedrich, *Metallurgie*, 1908, **5**, 529.

of *Scheele's green.* The salt forms a blue-coloured solution in caustic potash which is quickly decomposed on heating, with separation of copper oxide.

Arsenates of Copper.—These salts correspond closely to the phosphates, and several basic salts occur in the mineral kingdom. The *ortharsenate* $Cu_3(AsO_4)_2,2H_2O$ is obtained as a blue amorphous powder by heating together copper nitrate and calcium arsenate. Olivenite, $Cu:AsO_4.Cu.OH$, crystallises in olive-green or brown rhombic prisms, and can be obtained artificially by heating a solution of the ortharsenate to 100°.

Clinoclasite, $AsO_4(CuOH)_3$, forms dark green monoclinic prisms possessing a pearly or vitreous to resinous lustre.

Carbonates of Copper.—We are only acquainted with basic copper carbonates. Of these, two occur in large quantity in the mineral kingdom. Malachite, $CuCO_3,Cu(OH)_2$, forms monoclinic, frequently twin, crystals which are rarely perfectly developed, simple crystals being seldom found. It also occurs massive with botryoidal or stalactitic surface, often fibrous and frequently granular or earthy. Its colour is a bright green, and its specific gravity varies from 3·7 to 4·01. Green malachite accompanies other ores of copper, occurring especially in the Urals, at Chessy in France, in Cornwall and Cumberland in England, and at the copper mines of Nischne-Tagilsk. The fibrous varieties are frequently deposited in different coloured layers which take a high polish, and from these masses vases and other ornamental articles are manufactured. Crystals of malachite can be obtained artificially by allowing a piece of porous limestone to lie in a solution of copper nitrate having a specific gravity of 1·1, until the stone becomes covered with basic nitrate, and then bringing it into a solution of sodium carbonate having a specific gravity of 1·04, when after a few days malachite crystals are formed (Becquerel).

Verdigris, or copper rust, formed by the joint action of air and water on copper, possesses the same composition as malachite.

Azurite or *Azure Copper Ore*, $2CuCO_3,Cu(OH)_2$, occurs together with malachite and other copper ores in shining monoclinic tablets or short prisms, and also as an amorphous or earthy mass having a dark azure-blue colour. It possesses a specific gravity of 3·5 to 3·83. If crystallised copper nitrate be heated with pieces of chalk under a pressure of from 3 to 4 atmospheres a crystalline warty mass of azurite is formed

(Debray). Azurite dissolves in a hot solution of sodium bicarbonate and the solution on boiling deposits a green powder of malachite.

The following carbonates have also been isolated,[1] $5CuO,CO_2$, a blue bulky precipitate obtained by the precipitation of copper salts by sodium carbonate; $5CuO,3CO_2$, a light blue stable precipitate obtained by precipitation with sodium hydrogen carbonate, and $8CuO,3CO_2,6H_2O$, a dark blue substance obtained by the action of water on the double carbonate of copper and sodium.

Silicates of Copper.—Two silicates of copper occur as minerals. *Dioptase* or *emerald copper*, H_2CuSiO_4, is found in compact limestone in the Kirghese Steppes and also in Siberian gold-washings. It forms emerald-green hexagonal crystals (class 17, p. 201), having a specific gravity of 3·3.

Chrysocolla, H_2CuSiO_4,H_2O, exists as a bluish botryoidal mass occurring with other copper ores. The name of chrysocolla occurs in old writers and serves to describe the most diverse bodies. The word originally was used to signify the substance employed for soldering gold (*χρυσός*, gold, and *κολλάω*, to cement); this, being prepared from urine, was probably microcosmic salt, which became coloured blue in the act of soldering gold to copper or brass. The word then came to be used for any green or blue substance, especially such as contained copper; the confusion thus created was great, all blue or green minerals, such as emerald and malachite, as well as substances which were employed for soldering, being termed chrysocolla. Brochant, in the year 1808, first proposed to confine the use of the name to this particular mineral.

Ammoniacal Compounds of Copper.

211 By the action of ammonia on both cuprous and cupric salts, a large number of compounds have been obtained, the empirical formulæ of which show that combination has taken place between the copper salt and a varying number of molecules of ammonia. As to the manner in which the combination takes place, and the exact constitution of the products, very little is at present known, and they are usually formulated as additive compounds or in accordance with Werner's co-ordination theory.

[1] Pickering, *Proc. Chem. Soc.*, 1909, **25**, 188. See also Gröger, *Zeit. anorg. Chem.*, 1900, **24**, 127.

Many other metals form similar series of ammoniacal derivatives, these being often more complex than in the case of copper, as for example those of cobalt and platinum. The compounds appear to be formed chiefly by the metals occurring in the middle of Mendeléeff's double periods (p. 52).

The ammoniacal cuprous compounds are colourless when pure, but very readily undergo oxidation, yielding the corresponding ammoniacal cupric salts, which usually have a deep blue colour and yield solutions of the same colour. The most important of these are the derivatives of cupric chloride and sulphate.

Cuprous Ammonium Sulphate.—Colourless crystals of the composition $Cu_2SO_4,4NH_3,H_2O$ have been obtained by passing a weak electric current through a strongly ammoniacal solution of cupric sulphate.[1] In moist air this substance changes rapidly to copper and a cupric compound.

The compound $Cu_2SO_4,4NH_3$ is precipitated as a white crystalline powder on the addition of alcohol to a solution of cuprous oxide and ammonium sulphate in aqueous ammonia at 50° in an atmosphere of hydrogen.[2]

Cupric Chloride and Ammonia.—Anhydrous cupric chloride absorbs ammonia, increasing in bulk and forming a blue powder having the composition $CuCl_2,6NH_3$; this gradually dissociates first into $CuCl_2,4NH_3$, and then further to $CuCl_2,2NH_3$.[3]

When ammonia is passed into a hot saturated solution of cupric chloride a dark blue solution is formed, which, on cooling, deposits small dark blue octahedra or pointed tetragonal prisms of *cuprammonium chloride*, $CuCl_2,4NH_3,2H_2O$.[4] It is converted at 150° into $CuCl_2,2NH_3$, which is a green powder, and on further heating decomposes as follows:

$$6(CuCl_2 2NH_3) = 6CuCl + 6NH_4Cl + 4NH_3 + N_2.$$

Water converts it into cuprammonium chloride, ammonium chloride, and a basic cupric chloride having the composition $CuCl_2,4CuO,6H_2O$.

Cupric Sulphate and Ammonia.—When a solution of copper sulphate is treated with ammonia a basic sulphate is first thrown down. On further addition of ammonia this dissolves to a deep pure blue liquid containing *cuprammonium sulphate*,

[1] Foerster and Blankenberg, *Ber.*, 1906, **39**, 4428.

[2] A. Bouzat, *Compt. rend.*, 1908, **146**, 75.

[3] Bouzat, *Compt. rend.*, 1902, **135**, 292; *Ann. Chim. Phys.*, 1903, (7), **29**, 305.

[4] Sabbatani, *Ann. Chim. Farm.*, 1897, **26**, 337.

$CuSO_4,4NH_3,H_2O$, which was first described by Stisser in 1693 as an *arcanum epilepticum*, and afterwards termed *cuprum ammoniacale*. In order to obtain this compound in fine crystals a layer of strong alcohol is poured on to the concentrated aqueous solution and the whole allowed to stand: in this way very long and thin transparent azure-blue rhombic prisms are deposited. These on exposure to the air lose ammonia and are gradually transformed into ammonium sulphate and basic copper sulphate. Heated gently to 150° an apple-green powder of the composition $CuSO_4,2NH_3$ is obtained. Anhydrous copper sulphate absorbs dry ammonia gas with evolution of heat forming a fine blue powder consisting of $CuSO_4,5NH_3$, which like the foregoing compound on heating to 200° forms the compound $CuSO_4,NH_3$ (Graham).

It will be noticed that in several of these compounds the total number of molecules of water and ammonia in combination with the copper sulphate molecule is five, and they may therefore be regarded as crystallised copper sulphate, $CuSO_4,5H_2O$, in which either the whole or a certain number of the water molecules have been replaced by an equal number of ammonia molecules. The same relation is found still more prominently in the ammoniacal compounds of some of the other metals.

Detection and Estimation of Copper.

212 The halogen compounds and nitrate of copper colour the non-luminous gas flame green, and the same coloration is obtained from the other salts when mixed with a chloride or moistened with hydrochloric acid.

The spectrum of this flame is a banded one containing a large number of lines of which two in the violet, lying between the rubidium and cæsium lines, are the most characteristic. The spark spectrum of cupric chloride is also rich in lines and contains very bright lines in the green (Lecoq de Boisbaudran). When borax is moistened with any copper salt and heated in the oxidising flame a bead is obtained which, when hot, is green, and when cold possesses a blue colour; in the reducing flame, especially with the addition of a small quantity of tin or a tin compound, the bead becomes red and opaque with separation of cuprous oxide or metallic copper. Copper salts are thrown down by sulphuretted hydrogen in the form of a brownish-black precipitate of cupric sulphide, CuS, which is slightly soluble in

ammonium sulphide, but not in freshly prepared potassium or sodium sulphide. The precipitated sulphide dissolves readily in warm dilute nitric acid forming a clear blue solution which assumes a fine dark blue colour on the addition of ammonia. Copper can also easily be detected by the reduction to the red metallic bead on charcoal before the blowpipe, or upon the charred end of a lucifer match (Bunsen's test).

Copper is estimated quantitatively either as oxide, sulphide or metal. For the purpose of estimating it as oxide, the boiling solution of the copper salt is treated with a slight excess of pure potash or soda, the precipitate repeatedly washed by decantation with boiling water, then thrown on to a filter, again washed, dried, and ignited.

Very satisfactory results are obtained by the electrolytic deposition of the metal, this method being especially advantageous where a large number of determinations have to be made daily, as is the case in a copper works. The copper solution may be electrolysed in a platinum basin which acts as the cathode, the anode being a platinum wire. The copper is thus deposited on the basin; it is washed by decantation with water, then with a little alcohol, dried and weighed together with the tared basin.

Copper is often estimated volumetrically by adding potassium iodide to a solution of the sulphate, and estimating the iodine liberated by titration with standard sodium thiosulphate, or by the titration of the ammoniacal solutions of the copper salts with potassium cyanide solution.

Atomic Weight of Copper.—By the reduction of precipitated copper oxide with hydrogen Berzelius[1] obtained the number 63·30, whilst Erdmann and Marchand[2] by the same method obtained the number 63·46. Hampe,[3] by the reduction of the oxide and by the electrolysis of pure copper sulphate, obtained a number almost identical with that of Berzelius, viz., 63·31. The careful experiments of Richards have shown that all these numbers are too low, the error being due to the fact that copper oxide contains occluded nitrogen and oxygen, and that copper sulphate cannot, as previously supposed, be completely dehydrated at 255°. Richards therefore determined the atomic weight by the analysis of pure cupric bromide, the amount of silver required for complete decomposition of the bromide and

[1] *Pogg. Ann.*, 1826, **8**, 177. [2] *Journ. pr. Chem.*, 1844, **31**, 380.
[3] *Zeit. anal. Chem.*, 1873, **13**, 352.

also the weight of the silver bromide formed being ascertained. The average of the results gave the number 63·57 for the atomic weight of copper. From the sulphate he obtained the number 63·55,[1] while the number now adopted (1913) is 63·57.

SILVER (ARGENTUM). Ag = 107.88.

213 Silver has been known from the earliest times, and the oldest names by which it was designated referred to its bright white colour; thus in the Hebrew, Késeph, the root signifies to be pale, whilst the Greek word ἄργυρος, silver, is derived from ἀργός, shining. The alchemists termed silver Luna or Diana, and it is often represented by the symbol of the cresent moon.

Silver occurs frequently in the native state, and is sometimes found in considerable quantity; thus, in the museum at Copenhagen there is a mass of native silver found at Kongsberg in Norway which weighs a quarter of a ton, and in South Peru masses have been found which weigh more than 8 cwt., whilst at Idaho, at the "poor man's lode," large masses of native silver have also been obtained. Native silver usually contains gold, copper, and sometimes mercury and other metals.

The most important ores of silver are: argentite or silver-glance, Ag_2S; pyrargyrite, ruby-silver, or dark-red silver, Ag_3SbS_3; stromeyerite or silver-copper glance, $(Ag,Cu)_2S$; stephanite, Ag_5SbS_4; polybasite, $(Ag,Cu)_9(Sb,As)S_6$; chlorargyrite or horn-silver, AgCl. Of less importance are proustite or light-red silver ore, Ag_3AsS_3, dyscrasite, Ag_4Sb, silver bromide, AgBr, silver iodide, AgI, and others. Silver also occurs in sea-water, a fact which was known to Proust in the year 1787.

214 *Metallurgy of Silver.*—Metallic silver is obtained from its ores by four different processes; either it is alloyed with lead, and then the lead is removed by oxidation, or it is amalgamated with mercury and this removed by distillation, or it is brought into combination with copper sulphide by smelting with pyritic copper ores, and the argentiferous matte produced is treated by a wet method, or reduced to metallic copper which is refined by the electrolytic process, or lastly it is brought into solution as a salt and precipitated. The practical adoption of one

[1] Numerous papers in *Chem. News*, 1891–2, **63**, **65**, **66**.

or other of these processes depends upon the nature of the ore, the position of the mine, and the price of the labour, fuel, &c.

It was by the first of these methods that the ancients extracted silver from its ores, and this remained for long the only known process. Strabo describes the method adopted in Spain for this purpose. The washed ore was melted with lead, and after this was got rid of (*ἀποχυθέντος τοῦ μολύβδου*), the pure silver remained behind. Pliny also, though he did not understand the nature of the operation, states that in order to obtain pure silver the ore must be cupelled together with lead; concerning the silver ore he says, "excoqui non potest, nisi cum plumbo nigro aut cum vena plumbi—et eodem opere ignium descendit pars in plumbum, argentum autem innatat, ut oleum aquis," this being an indistinct statement of the mode in which metallic silver separates from the oxidised slag. This process was termed in the works attributed to Basil Valentine "Saigern" or "eliquation."

The Cupellation Process.—In this process the silver ores are first converted into an alloy of lead and silver by smelting with lead ores, which reduces the silver to the metallic state, the excess of lead combining with it to form an alloy. The metallic lead obtained from galena always contains silver in small quantities, and from this a quantity of lead rich in silver is obtained by the Pattinson or Parkes process (see under Lead). To obtain the silver free from lead in both cases the alloy is subjected to the process of cupellation, the lead being oxidised to litharge, which is removed, leaving the silver in the metallic state. For this purpose there are many different forms of furnace, modes of refining, &c., in use, but only two distinct methods of cupellation are employed, viz.: (1) the English, and (2) the German system.

(1) *The English Process.*—The peculiarity of this system is that the cupel or porous hearth or test upon which the oxidation takes place is movable, and the lead is added at intervals.

Figs. 116 and 117 show the construction of the English cupellation furnace or refinery. Fig. 116 shows a transverse section through the test, and Fig. 117 a plan and sections of the test and test frame.

The refinery consists essentially of a reverberatory furnace. The metal to be refined is placed upon the hearth, or cupel, or test (E), which consists of an oval wrought-iron frame (AA',

Fig. 117) about five feet long and two and a half feet wide, crossed by five iron bars (*a*).

Formerly this frame was filled with finely-powdered bone-ash moistened with a little water in which a small quantity of

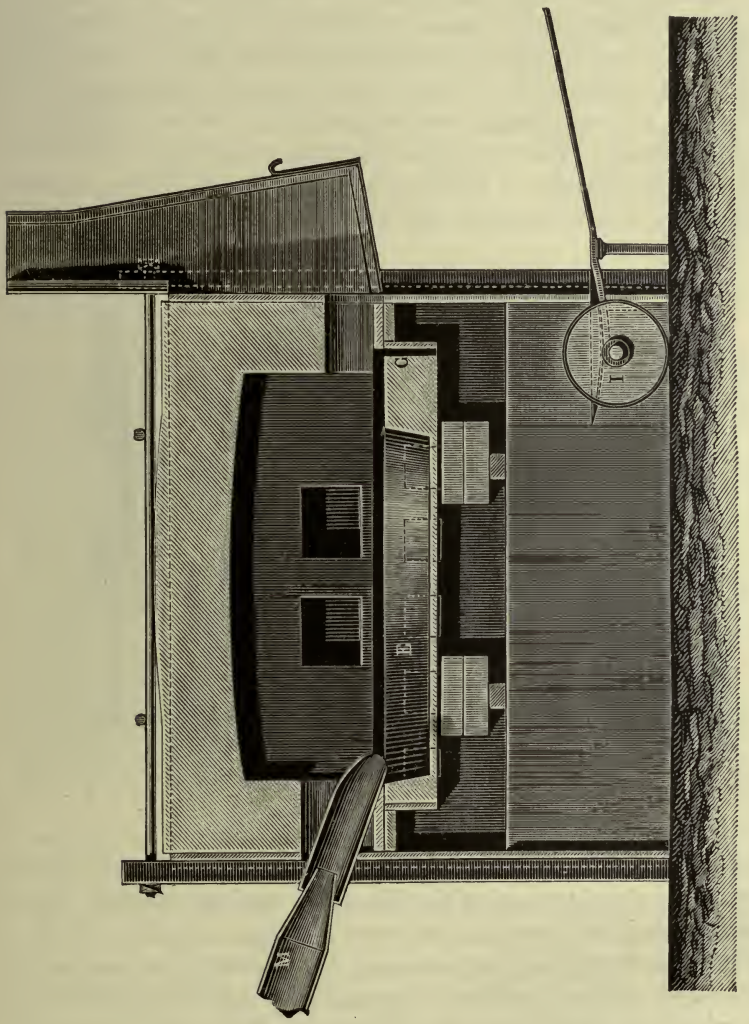


Fig. 116.

potassium carbonate had been dissolved. This was well solidified by beating, and scooped out until it was an inch thick and had the form shown in the figure.

At the present time, marl, similar in composition to that used in the German furnace, barytes, or cement, or various

mixtures of cement and fireclay, are often used for the first stage of the process, bone-ash or barytes being employed for the final stage.

In forming the test, a flat rim is left all round about two inches wide, except at one end (E, Fig. 117), called the front or breast of the cupel, where it is five inches wide, and through this a channel (G) connecting the bed of the cupel with the slot (G′) is cut to allow the melted oxide of lead to flow out into the waggon (I) beneath, without coming into contact with the iron, which it would corrode. The cupel thus arranged is wedged up into its place in the furnace, of which it forms the hearth (E, Fig. 116), and where it is so arranged that the flame from a coal fire lying

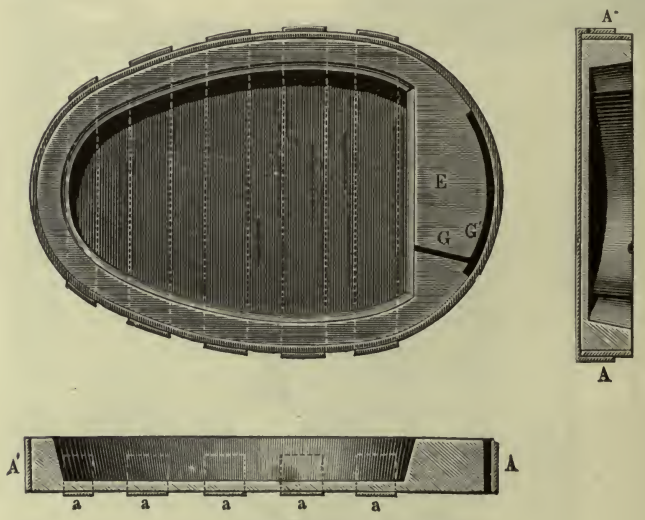


Fig. 117.

on the bars plays over its surface, and the products of combustion escape through two flues. A blast of air from the nozzle or tuyere (M, Fig. 116) enters the furnace at the side opposite that against which the breast of the cupel is placed, a current of air being thus blown over the surface of the lead at the rate of about 200 cubic feet per minute. Opposite the door is a hood for carrying the fumes into the chimney. The temperature is gradually raised to redness, and the cupel is almost filled with the lead to be treated, which is ladled in from an iron pot where it has been previously melted by means of a fire placed beneath. Fresh lead is added from time to time to supply the place of that which is oxidised, until at length a quantity of

lead originally amounting to about five tons is reduced to between two and three cwt. This metal is withdrawn by making a hole through the bottom of the cupel; the aperture is afterwards closed with fresh bone-ash or marl, and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3,000 to 5,000 ounces of silver, or from 93 to 155 kilos., has been thus obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification of the concentrated silver-lead separately, because in the last stages of the operation the litharge carries a good deal of silver with it; these portions of

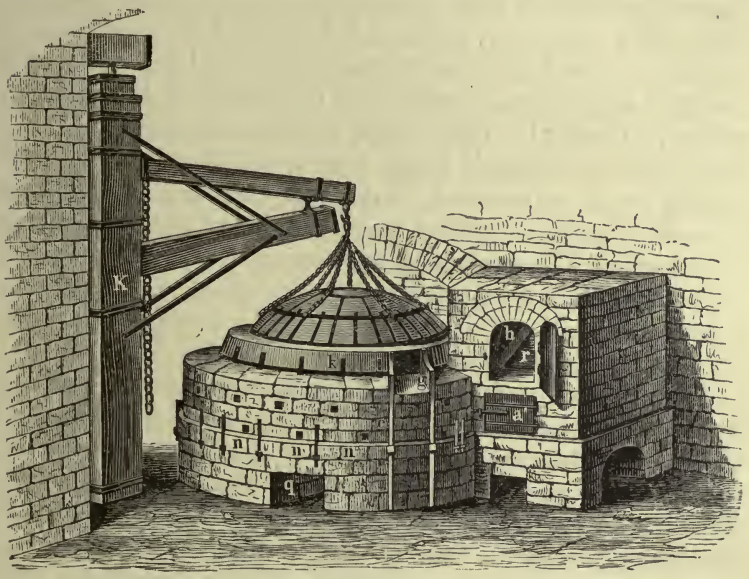


Fig. 118.

litharge, therefore, after being reduced, are again subjected to the desilverising process.

(2) *The German Cupellation Process.*—This differs from the English process inasmuch as the hearth is always formed of marl instead of bone-ash, and the process is completed in one operation. The natural marl used consists of about 65 per cent. of limestone and 30 per cent. of clay, together with 5 per cent. of magnesium carbonate and oxide of iron.

The hearth is made of large dimensions, and the whole of the charge is placed on the cupel at once. The furnace used for this purpose is shown in Fig. 118. The circular cover *k* is movable

for the purpose of renewing the cupel. When all is ready, straw is thrown upon the hearth, on to which the pigs of rich lead are placed; the cover *k* is then lowered and the joints made good with clay; the fire is lighted, and as soon as the lead is melted its surface becomes covered with a dark crust termed "abzug," consisting of the oxides of foreign oxidisable metals and other impurities in the lead; this crust is skimmed off through the working door (*g*); the heating is regulated so as to maintain the lead at a dark-red heat, until the impurities cease to separate in the form of scum. The next product which appears is known as "abstich," or impure litharge, and at the end of two hours the formation of the pure litharge begins, the temperature being kept up at a cherry-red heat until the operation is complete. Just before the last portions of lead are removed a beautiful appearance, known as the fulguration of the metal, is noticed. During the early stages of the operation the film of lead oxide is constantly being formed, and this is renewed as rapidly as it is removed; but when the lead has all been oxidised, the film of litharge becomes thinner and thinner, and as it flows off a succession of beautiful iridescent tints due to the colour of thin films (Newton's rings) is observed, and after a few moments the film of oxide suddenly disappears and the brilliant surface of the metallic silver is seen beneath.

The Mexican Amalgamation Process.—Although the ancients were well acquainted with the fact that mercury dissolves gold and silver, it does not appear that they applied this knowledge to the extraction of silver from its ores. This was first done in Mexico in the year 1557 by Bartholomeo de Medina, and applied on the large scale in the year 1566. The same process was employed at Potosi in Peru in 1574, and fully described in 1590 by Joseph Acosta, in his *Historia natural y moral de las Indias.* The identical method is still carried on to some extent in Mexico, Peru, and Southern Chili. The ores which are worked by this process contain metallic silver, sulphide of silver, chloride of silver, &c., these substances being distributed in small masses through large quantities of gangue, thus rendering it difficult or impossible to separate the ore by washing.

The first operation in the process, which has to be carried on in a country devoid of fuel and running water, and where, therefore, neither steam nor water-power can be obtained, is the fine division of the ore. This is effected by stamping and grinding mills worked by horse or mule power, and termed *arrastra.*

Into these water and ore are brought and ground together to a fine mud between blocks of porphyry fastened to an axis which is turned by the mules; the wet and powdered ore is then brought on to a paved floor termed a *patio*, and mixed with from 3 to 5 per cent. of common salt, and the salt thoroughly incorporated with the mass by the treading of mules. After standing for a day, mercury is added together with a substance termed *magistral*, an impure mixture of cupric and ferric salts. As soon as the magistral has been added, more mercury is poured on, and the heap or *torta* is again trodden by mules to bring about a thorough incorporation of the ingredients and thus to effect the chemical decomposition which their contact entails. The treading of the torta is generally performed by mules which are blindfolded and tied together four abreast; one mule for every two montones (about three tons) is required at Guanaxuato for the effectual treading of a heap. A driver, who stands in the centre of the torta, guides the animals with a long halter, causing them first to tread at the outer edge, and gradually diminishing the radius of the circle described. The time necessary for working a torta varies from fifteen to forty-five days according to circumstances (Phillips).

As soon as the amalgamation is found to be complete, the slimy mass is washed in buddles worked by mules, the lighter particles of mud washed away, and the heavier amalgam deposited. The amalgam is next filtered through canvas bags to remove excess of mercury, and is then distilled by being placed under a large iron bell luted at the bottom with water, round the upper part of which a charcoal fire is lighted. The silver which is then left behind, and is termed *plata piña*, possesses a white frosted appearance, and is fused into bars in the usual way.

The chemical reactions which occur in the process have been investigated by Boussingault, Karsten, and other chemists, but in spite of their investigations there still remains some degree of doubt respecting the exact nature of the reaction.

The following is the probable explanation of the chemical changes which occur. The first reaction is a double decomposition between the sulphates of iron and copper and chloride of sodium with formation of the chlorides of the metals. These decompose silver sulphide into silver chloride:

$$2CuCl_2 + Ag_2S = 2CuCl + 2AgCl + S.$$

The cuprous chloride thus formed dissolves in common salt and acts further upon the sulphide :

$$2CuCl + Ag_2S = Cu_2S + 2AgCl.$$

The solution of the silver chloride in common salt is then decomposed by the metallic mercury with formation of calomel and metallic silver. All the mercury which is thus converted into calomel is lost, and it amounts to about double the weight of the silver obtained.

Since 1904, the Mexican process has been largely displaced by the introduction of fine-grinding in tube-mills in conjunction with a modification of the cyanide process.

The American or *Washoe Amalgamation Process.*—Owing to the scarcity of fuel and labour in the Nevada districts, where large quantities of both rich and poor silver ores occur, it is found impossible to work the ordinary methods, because a process necessitating the preliminary roasting of the ore cannot be carried on, and the loss of mercury in the Mexican process is too great to render that method applicable to the large quantity of poor ore which the district yields.

This necessity has led to the invention of a process of amalgamation in iron pans, which is called, from the name of the district, the Washoe process. The richer ores of the Nevada mines contain many other metals, and are usually roasted with common salt in reverberatory furnaces and then amalgamated in barrels. The poor ore, on the other hand, after having been stamped to powder, is ground in cast-iron pans together with mercury and hot water, with or without the addition of common salt and copper sulphate. The amalgam is next washed, strained in bags, and distilled in carefully constructed cast-iron retorts, and the silver which remains melted and cast into ingots. The chemical changes which occur in this process of amalgamation are similar to those taking place in the Mexican operation, but as the ore contains a considerable proportion of native silver, the presence of a copper salt is not so necessary, as under the influence of heat and friction mercury and iron alone are capable of extracting the silver. The loss of mercury in the Washoe method is much less than in the older amalgamation operations, as it is chiefly mechanical, no mercury salt being formed.

A third amalgamation process is known as the Boss continuous process in which the ore is first crushed in a stamp-mill and

the pulp finely ground in pans. After this, it is caused to pass through a series of amalgamating pans, often ten in number, placed side by side, each pan having an overflow pipe, through which the pulp flows into the next one of the series. From these it is passed through a series of settlers arranged in the same manner, in which any mercury or amalgam passing over settles and is collected. By this process the labour of conveying the pulp to the pans is avoided, and the ore is kept in contact with mercury for a longer period.

215 *Extraction of Silver in the Wet Way.*—Several of these processes have now been generally adopted.

Ziervogel's process, carried on in Saxony and other places, depends upon the fact that the silver in compounds of silver, copper, and iron sulphide may be converted into silver sulphate by careful roasting, while the iron and copper are converted into oxides. The silver sulphate is readily soluble in hot water and is extracted by lixiviation in wooden vats, the silver being precipitated from this solution in the metallic state by treatment with metallic copper. Ores are seldom treated by the Ziervogel process as they are not sufficiently rich, but the process is admirably suited to argentiferous copper mattes obtained from the smelting of argentiferous pyrites. These mattes are first ground and then subjected to a preliminary roast, during which ferric sulphate is first formed together with copper and iron oxides. When the temperature is raised the ferric sulphate is decomposed, sulphuric anhydride being evolved, which brings about the formation of copper sulphate. After about five hours the charge is withdrawn, and consists of a mixture of ferric oxide, cuprous and cupric oxides, silver sulphide, and copper sulphate. This charge is prepared for the "final" or "sulphating" roast by fine grinding, and is charged into a gas-fired, double-hearthed reverberatory furnace. The temperature is carefully regulated so that copper sulphate is decomposed, silver sulphate formed, and any cuprous oxide present converted into cupric oxide; the charge is then withdrawn and allowed to cool, and is ready for lixiviation.

Augustin's Process.—This method was formerly employed for argentiferous copper regulus and for argentiferous ores. These are roasted to remove excess of sulphur, and then heated with 5 per cent. of common salt, the silver chloride thus formed extracted by a hot saturated solution of salt, and the silver deposited from the solution by the action of metallic copper.

As silver chloride is much more easily dissolved by a solution of sodium thiosulphate than by brine, the Augustin process is now only used in conjunction with the Patera process (see below), and is not as a rule used for working up argentiferous mattes or other products.

Percy-Patera Process.—Another wet process depends upon the following reactions, first suggested by Percy, and afterwards carried out by von Patera. The argentiferous ore is first roasted with common salt, by which the silver is converted into the chloride as in the Augustin process; this is then dissolved out by a cold dilute solution of sodium thiosulphate:

$$2AgCl + 3Na_2S_2O_3 = Ag_2S_2O_3,2Na_2S_2O_3 + 2NaCl.$$

The silver in solution is precipitated by means of a solution of sodium sulphide, whereby silver sulphide is formed and sodium thiosulphate regenerated according to the following equation:

$$Ag_2S_2O_3,2Na_2S_2O_3 + Na_2S = Ag_2S + 3Na_2S_2O_3.$$

Gold, copper, and any other heavy metals in solution are precipitated with the silver. Care is taken to add only sufficient sodium sulphide to precipitate the metals, as the liquors are used over and over again for the extraction of fresh ore. The sulphide precipitate is collected in a filter press, dried, roasted in a muffle, and charged into a bath of hot lead, the rich argentiferous lead thus obtained being afterwards cupelled.

Russell Process.—This consists in leaching the ores by a solution of sodium-copper thiosulphate, which dissolves any gold or silver in the metallic state, and any sulphide, arsenate, or antimonate of silver which is not readily attacked by sodium thiosulphate alone. It is therefore chiefly used as an auxiliary to the Patera process, the extraction with the thiosulphate of sodium solution being followed by an extraction with the double thiosulphate. The metals in solution are precipitated by means of sodium sulphide, and the precipitate treated with hot concentrated sulphuric acid in cast-iron vessels. This dissolves the silver and copper present, leaving any gold behind. From the solution the silver is precipitated by means of copper, and the resulting copper sulphate used for making fresh leaching liquors.

Claudet's Process.—The burnt pyrites of the sulphuric acid makers contains, as we have seen, not only copper, but also a small quantity of silver, which occurs in the cupreous liquors in the form of chloride dissolved in the excess of common salt. Although the quantity of silver in the burnt ore does not often exceed 12 dwts. to the ton, it is found possible to obtain this economically in the form of insoluble silver iodide by adding a solution of iodide of potassium, sodium, or zinc to the tank liquor, a small trace of gold being at the same time precipitated. The precipitate is reduced to the metallic state by means of zinc in the presence of hydrochloric acid, metallic silver being formed together with zinc iodide, which may be used to precipitate a further quantity of silver. The results obtained at the Widnes Metal-works by this process show that between 150 and 300 grains of silver and between $1\frac{1}{2}$ and 3 grains of gold may be extracted from each ton of ordinary Spanish pyrites.

The Cyanide Process.—The solvent action of solutions of potassium or sodium cyanide on silver minerals has been applied with considerable success in Mexico and other countries. The process consists in the fine grinding or sliming of the ore, agitation by mechanical or aërial agitators with cyanide solution stronger than that used in the extraction of gold (0·7 per cent. instead of 0·3 per cent.), filtration of the silver-bearing solution from the slime and precipitation of the metallic silver by means of zinc.

Argentiferous Copper.—Much silver is also obtained by the treatment of argentiferous copper by an electrolytic refining process, the copper having been reduced from argentiferous copper pyrites, or obtained by Bessemerising the copper mattes obtained from the pyritic smelting of mixtures of pyritic copper ores and argentiferous materials (see Copper).

Electric Refining of Silver.—Large quantities of silver are refined by the Moebius process, in which the electrolyte consists of a silver nitrate solution containing about one per cent. of free nitric acid. Silver is deposited on the cathode and gold is left insoluble. Copper is not allowed to accumulate in the electrolyte to more than 4 or 5 per cent.

The Total Production of Silver during 1911 throughout the world is given in the following table, expressed in ounces.[1]

[1] *Mineral Industry*, 1911, **20**, 284.

United States of America	57,796,117	Greece	803,768
Australasia	17,109,503	France	1,607,535
Mexico	87,078,764	United Kingdom	493,720
Russia	160,753	Canada	33,486,938
Germany	14,132,805	Argentina	135,000
Austria-Hungary	1,851,880	Colombia	914,630
Belgium	8,037,675	Bolivia	4,179,591
Italy	643,014	Chili	1,500,000
Spain	4,179,591	Peru	8,037,675
Japan	4,822,605	Central America	2,345,000
Dutch Indies	515,250	Africa	1,100,000
		Other Countries	976,966
TOTAL			251,908,780

216 *Preparation of Pure Silver.*—The purest silver which occurs in commerce contains traces of other metals. Stas's classical researches on atomic weight determinations have shown how difficult it is to obtain any substance chemically pure, and this fact is especially well illustrated in the case of silver, a metal which possesses such characteristic reactions that one would suppose its separation in a state of chemical purity to be an easy task, and yet this is far from being the case.

Silver was obtained by Stas in a highly pure state by the reduction of carefully purified silver chloride by boiling with sodium hydroxide solution and sugar, by reducing silver nitrate solution with ammonium formate and acetate, and in several other ways. The precipitated silver was then dried by fusion with borax or lime. Stas's silver, however, probably contained a little occluded oxygen (Richard and Wells).

Samples of silver in a still purer state than those obtained by Stas have been prepared by Richards and Wells[1] for use in determinations of the atomic weights of chlorine and sodium. These investigators started with silver nitrate which was purified by repeated crystallisation from water; in one preparation as many as fifteen recrystallisations were performed. This was converted into silver chloride with pure hydrochloric acid, and the well-washed chloride reduced to metallic silver by warming with a solution of chemically pure caustic soda and

[1] A revision of the atomic weights of sodium and chlorine; *J. Amer Chem. Soc.*, 1905, **27**, 459.

invert-sugar. The precipitate of silver was then washed with water, dried, and fused on pure lime. In this way a button of extremely pure silver was obtained. This was then further purified by making it the anode of an electrolytic cell containing a concentrated solution of silver nitrate obtained from the same preparation of silver. The cathode was a wire of pure silver and upon this crystals of electrolytic silver were deposited. These crystals were dried and fused on a boat of pure lime in an atmosphere of hydrogen to remove any occluded oxygen. The bars of silver, so formed, were freed from lime by rubbing with sand, and washed, first with dilute nitric acid, then with ammonia to remove any silver nitrate, and finally with water. They were then dried by heating in a vacuum at 400°, in a hard glass tube.

Richards and Wells also prepared pure silver by dissolving commercial fine silver in dilute nitric acid, and reducing the nitrate, after recrystallising several times, by boiling with ammonium formate. The white precipitate of silver was washed repeatedly with water until the washings showed no Nessler test, and was then fused in hydrogen, rubbed with sand and acid, and treated as above. In all this work vessels of silver were used whenever possible in order to prevent contamination with other metals, and in other cases vessels of platinum, Jena glass, and fused quartz were employed.

Pure silver is used in the laboratory for volumetric analysis and for cupellation assays. It is not necessary for this purpose to have it so pure as the metal employed for atomic weight determinations, and it may be obtained sufficiently so by boiling well-washed silver chloride with caustic potash and sugar. The point of complete reduction is ascertained by taking a small portion out, washing it well with water, and dissolving in pure dilute nitric acid; if the reduction be complete it will dissolve without residue. The metal is then melted in a crucible together with some pure sodium carbonate or borax.

Molecular silver, employed in organic chemistry, is obtained, according to Wislicenus, by bringing zinc into contact with finely-divided silver chloride which has been precipitated in the cold and washed until nearly free from acid. In a few hours the chloride is completely reduced, and the precipitated silver may be separated from the sheet zinc by washing, and then treated with diluted hydrochloric acid to remove every trace of zinc. It is then brought on to paper and dried in the air, and

afterwards gently heated to 150°. Thus prepared it is a grey powder, possessing no metallic lustre, which, however, it assumes when rubbed under a burnisher or heated to redness.

217 *Properties.*—Silver possesses a pure white colour, and takes a high polish. Of all the metals it is the best conductor of heat and electricity; it is very tough and malleable, since 0·1 gram can be drawn out into a wire 180 m. in length, and silver leaf can be beaten out to a thickness of 0·00025 mm. In the finely-divided state, as obtained by the reduction of the chloride and other salts, silver presents the appearance of a dull dark-grey powder.

Silver is precipitated in very thin films in the form of a lustrous metallic mirror-like deposit on glass from ammoniacal solution in presence of many reducing agents, especially organic substances; it then adheres to the glass and transmits blue light.

Metallic silver is found native in regular octahedra, which frequently occur twinned, and also in dendritic forms. It is also often found in the crystalline form in silver smelting furnaces.

Silver fuses at a temperature of 962° in the absence of air, and at 956° in the presence of air. In the liquid state it possesses the power of absorbing oxygen from the air, which it gives up on solidification. When a mass of the metal is rapidly cooled the silver solidifies before the oxygen has escaped from the interior; this gas then bursts through the crusts, and drives out part of the fused silver in globular masses and excrescences; this peculiar phenomenon is known as the "spitting" of silver. When charcoal powder is thrown on the surface of the metal the charcoal withdraws the absorbed oxygen, and consequently prevents silver from spitting. The same preventive effect is noticed when silver is fused under common salt, but when fused under nitre the spitting takes place. The presence of 5 per cent. of copper prevents the spitting of silver.

When silver is heated, and then allowed to cool while ozone is impinging on the surface, a black stain is formed due to partial oxidation.[1] The maximum effect is produced at 220° to 240°, and no stain is produced above 450°.

Silver begins to volatilise at a white heat, and when heated in a lime crucible by means of the oxyhydrogen blowpipe it may be readily made to boil. By this process Stas was able to distil fifty grams of pure silver in from ten to fifteen minutes;

[1] Manchot and Kampschulte, *Ber.*, 1907, **40**, 2891.

no residue whatever was left behind, and a portion of the vapour, which has a bright blue colour, was carried out by the current of oxygen gas, and rendered the air of the laboratory hazy, imparting to it a metallic taste. Distilled silver has a specific gravity of 10·4923 (Kahlbaum, Roth, and Siedler); fused silver has a specific gravity of from 10·424 to 10·511 (Holzmann); whilst silver which has been exposed to pressure under the coining press has a specific gravity of 10·57 (G. Rose).

Silver foil becomes slightly transparent in air at 240° and more so at higher temperatures;[1] heating, however, to 500° in hydrogen or charcoal powder does not produce transparency, showing that the presence of oxygen is necessary although the quantity of oxygen absorbed is very minute.

The vapour density of silver at 2,000° has been determined by Nernst's [2] adaptation for high temperatures of Victor Meyer's displacement method, the bulb in which the heating takes place being made of iridium coated inside with a mixture of zirconia and yttria, and heated by means of an electric current. In this way the molecular weight was found to be 107 and 111; silver therefore at this temperature is monatomic.[3]

Silver is often used in the laboratory for the preparation of chemical utensils, as this metal is not, like glass or platinum, attacked by fused caustic alkali.

Colloidal Silver.—By the action of different reducing agents such as sodium tartrate and citrate, ferrous sulphate, dextrin, and tannin, on solutions of silver salts, Carey Lea [4] obtained a number of different precipitates which he regarded as allotropic forms of silver. This view has, however, proved incorrect, and the differences between these bodies and metallic silver are readily explained by their fine state of division and by their invariably containing small amounts of the other products of the reactions. The precipitates readily dissolve in water to form colloidal *silver solutions*, or silver "sols," which are coagulated or re-precipitated by the addition of small amounts of electrolytes.

[1] Turner, *Proc. Roy. Soc.*, 1908, **A.**, **81**, 301.

[2] *Zeit. Elektrochem.*, 1903, **9**, 622. [3] von Wartenberg, *Ber.*, 1906, **39**, 381.

[4] *Amer. J. Sci.*, 1889 (3), **37**, 476; **38**, 47, 129: *Phil. Mag.*, 1891 (5), **31**, 238, 320, 497; **32**, 337; *Amer. J. Sci.*, 1894 (3), **48**, 343. See also Schneider, *Ber.*, 1891, **24**, 3370; 1892, **25**, 1164, 1281, 1440; Barus and Schneider, *Zeit. physikal. Chem.*, 1891, **8**, 278; *Ann. Phys. Chem.*, 1893, **48**, 327; Oberbeck, *ibid.*, 1892, **46**, 265, 353; 1893, **48**, 745; Blake, *Amer. J. Sci.*, 1903, [4], **16**, 282.

Solutions of colloidal silver may also be prepared by Bredig's method, which consists in passing an electric arc between poles of silver under water. In this way a brown solution is obtained which has the power of rapidly decomposing hydrogen peroxide.[1]

By heating silver nitrate with an alkaline solution of sodium lysalbate or protalbate, Paal[2] obtained a yellow solution of colloidal silver, and this on dialysing and concentrating on the water-bath yielded a deep brownish-black powder, readily soluble in water. This product, sometimes termed *collargol*, has been prepared containing as much as 93 per cent. of silver.

Colloidal silver may also be obtained by heating silver nitrate solution with formaldehyde and sodium silicate, and concentrating the mixture on the water-bath;[3] also by boiling ammoniacal silver nitrate solution with acraldehyde and a small quantity of gelatin solution. By this latter method, concentrated solutions of colloidal silver, having the colour of bromine, may be prepared which may be kept for years without losing their properties or changing colour;[4] and several other methods of preparing colloidal silver have been published.[5]

All the colloidal solutions described contain small amounts of other substances resulting from the original reactions, which are "adsorbed," *i.e.*, condensed on the silver particles, and cannot be completely removed. Even Bredig's solutions, which are not produced by a reaction but by disintegration of solid silver, are not pure, as they always contain oxides.

Silvering and Plating.

218 Objects made of copper, or of brass, bronze, German silver or similar alloy, are frequently silvered to give a bright and permanent surface to these metals. If the covering of silver be thick the goods are said to be plated; if thin, they are said to be silvered. Silvering may be effected in several ways, the following process, for example, being employed for

[1] Bredig, *Anorganische Fermente* (Engelmann, Leipzig, 1901).

[2] *Ber.*, 1902, **35**, 2206.

[3] Küspert, *Ber.*, 1902, **35**, 2815, 4066 and 4070.

[4] N. Castoro, *Gazz.*, 1907, **37**, 391.

[5] Lottermoser and von Meyer, *J. pr. Chem.*, 1897, **56**, 241; 1898, [ii.], **57**, 540, Lottermoser, *ibid.*, 1905, [ii.], **71**, 296; Gutbier and Hofmeier, *Zeit. anorg. Chem.*, 1905, **45**, 77. See also an Introduction to the Physics and Chemistry of Colloids, by Emil Hatschek (J. and A. Churchill).

silvering small articles such as pins, buttons, &c. For this purpose a solution of silver chloride in sodium sulphite or thiosulphate, or in common salt, or cream of tartar, is employed; a warm solution is used, and the silver is instantly deposited upon the metallic object.

The *plating* of copper is effected by polishing the surface of the ingot which is to be plated, and then placing upon it a strip of bright silver, the area of which is somewhat smaller than that of the copper; the compound ingot is then exposed to a temperature slightly below the fusing point of silver, and by hammering or rolling at this temperature the two metals are sweated together, as it is termed; no soldering is employed in this process; the ingot is then rolled until it is reduced to the required thickness.

Electro-deposition of Silver.—The process of electro-plating in silver was discovered by Wright and Parkes of Birmingham, in the year 1840. They were employed during that year in making experiments with a view of obtaining a bright and firm deposit of metallic silver by an electro-process similar to that by which Jacobi, Jordan, and Spencer had succeeded in obtaining the deposition of copper. Their attempts, however, were not completely successful, inasmuch as they either obtained only a very thin coherent film or else the whole of the silver was thrown down in the form of a grey powder. At this juncture Wright met with a passage in Scheele's *Chemical Essays* (pp. 404–406), which soon proved of the highest importance to the commercial success of his undertaking, by enabling him to obtain suitable deposits of silver and gold. Speaking of the solubility of the oxides and cyanides of gold, silver, and copper, Scheele says that, "if these calces (that is the cyanides of gold and silver) have been precipitated, and a sufficient quantity of the precipitating liquor be added in order to redissolve them, the solution remains clear in the open air, and in this state the aërial acid (that is, the carbonic acid of the air) does not precipitate the metallic calx."[1] Working with this idea, Wright first employed a solution of chloride of silver in potassium ferrocyanide, and quickly got a thick deposit of firm and white silver, a result which had never previously been obtained. Soon afterwards he found that the solution of silver cyanide in cyanide of potassium gave still better results; and, submitting his results to the well-known firm of G. R. and H.

[1] Gore, *Electro-Metallurgy*, p. 19.

Elkington, a patent was taken out, and this patent process proved to be the foundation of all electro-plating of gold and silver, because it included the solutions of the alkali cyanides, the only liquids which fulfil all the necessary conditions. The silver-plating solution consists of a solution of cyanide of silver in cyanide of potassium, an excess of the cyanide of potassium being added in order that no cyanide of silver shall separate out on the positive pole, which always consists of silver. The action which takes place in this electrolysis is the same as that described under copper electro-plating. The negative pole is connected with the object to be silvered, and upon this the silver is deposited, whilst at the positive pole the radical CN combines with the silver which forms the pole, and the cyanide of silver thus formed dissolves in the excess of potassium cyanide.[1]

Silvering of Glass Specula and Mirrors.—Many organic bodies such as milk-sugar possess the power of precipitating silver in the form of a highly coherent mirror when brought into contact with an alkaline silver solution.

ALLOYS OF SILVER.

219 The presence of small quantities of other metals, such as antimony, arsenic, bismuth, tin, or zinc, renders silver brittle and liable to crack when rolled. The alloys of silver and copper are the only ones which are largely used in the arts. Almost al commercial silver is alloyed with copper, as pure silver is too soft for ordinary purposes such as coining and jewellery work. The addition of a small quantity of copper imparts to it a sufficient degree of hardness, and makes it tougher as well as more easily fusible. Thus, for instance, a wire of pure silver having a sectional area of 1 sq. cm. breaks with a weight of about 2,800 kilos., whereas if it be alloyed with 25 per cent. of copper and drawn cold, it will sustain a weight of from 6,000 to 9,000 kilos.; after annealing it becomes soft, and breaks with a weight of from 3,800 to 4,800 kilos. It has been found that alloys of copper and silver, however perfectly the metals may be mixed and melted together, undergo on solidification a process of liquation, the upper and the lower portions of the ingot

[1] Further particulars respecting this interesting process will be found in Gore's *Electro-Metallurgy*.

differing in fineness from 0·002 to 0·015. Levol[1] has shown that the only alloy of these metals which does not exhibit this peculiarity is one having the specific gravity 9·9045, and containing 28 per cent. of copper, this is now recognised as the eutectic alloy of the series. The fineness of silver alloy is generally calculated upon a thousand parts; thus, for instance, the one above mentioned will have a fineness of 720. The colour of the silver-copper alloys becomes more and more red as the percentage of copper is increased, but an alloy of 1 part of silver and 4 of copper does not possess the true copper colour.

Silver Coin.—The proportion of copper in the standard silver used in different countries varies considerably. The English standard coinage silver contains 7·5 per cent. of copper, or has a fineness of 925; the specific gravity of the English silver is 10·30. In France three standard alloys are employed; one containing 950 per mille of silver for medals and plate; another containing 900 per mille for coin; and a third containing 800 per mille for jewellery work. In Germany and Austria the standard for coin contains 900 per mille of silver. The German alloy used for silver-plating contains from 700 to 810 per mille of silver.

The present composition of British silver coin is the same as that issued in the time of Edward I., the alloy in this reign containing 925 of fine silver and being described as "the old standard of England."

Up to the year 1851 the manufacture of coin was entrusted to a private company termed the moneyers, who had to produce coin varying within very narrow limits, the alloy thus produced being compared with plates of standard silver termed "standard trial plates." Since the above year, the business of coining has devolved upon the Government, the Chancellor of the Exchequer being Master of the Mint. The ancient ceremony of the "trial of the pyx" is, however, still carried on every year. This consists in a public trial by competent assayers appointed by the freemen of the Goldsmiths' Company of the coin (both gold and silver) issued during the year. By this means the accuracy of the coin both as to fineness and as to weight is ascertained, and this trial served in former days as the only safeguard against debasement of the coinage. The fineness of the coins is ascertained at the trial of the pyx by reference to the trial plates whose composition has been determined with the greatest accuracy.

[1] *Ann. Chim. Phys.*, 1849, [3], **26**, 220.

The following table gives the accurate composition of trial plates of various dates, portions of which have been preserved and analysed [1] in the Royal Mint. The plates made in former times, when no accurate means of analysis existed, show considerable variation in the composition of the silver standard plates, the standard prescribed by law being in each case the same, viz., 925 :—

Date	Fineness
1477	923·5
1560	930·2
1660	924·2
1728	928·9
1829	925·0
1873	924·96

COMPOUNDS OF SILVER.

Silver and Oxygen.

220 Silver forms two oxides :—

Silver oxide, Ag_2O.
Silver peroxide, AgO, or Ag_2O_2.

A third oxide known as silver suboxide was described by Wöhler,[2] who obtained it by acting on different silver salts with hydrogen, and by heating silver citrate in hydrogen, and treating the solution of the residue, which he supposed to contain silver subcitrate, with caustic potash. Further investigations by Bailey and Fowler[3] and by Muthmann have shown that such an oxide does not exist, the substance thus described being a mixture of silver and silver oxide.[4] The peculiar red colour of the supposed solution of silver subcitrate is due to very finely divided silver.

Silver Oxide, Ag_2O.—This is the best defined oxide of silver and is obtained by precipitating silver nitrate with pure potash or soda. Thus prepared it forms a brown precipitate, which when dried at a temperature of from 60 to 80°, becomes almost

[1] Roberts, *Journ. Chem. Soc.*, 1874, **27**, 197.
[2] *Annalen*, 1839, **30**, 1. [3] *Journ. Chem. Soc.*, 1887, **51**, 416.
[4] See also Lewis, *J. Amer. Chem. Soc.*, 1906, **28**, 139 ; Luther and Pokorny, *Zeit. anorg. Chem.*, 1908, **57**, 290.

black. When freshly precipitated silver chloride is boiled with an excess of caustic potash, the same oxide is obtained in the form of a finely divided bluish-black powder. It is soluble in 15,360 parts of water at ordinary temperatures,[1] imparting to the solution a metallic taste and an alkaline reaction. In the moist condition it absorbs carbon dioxide from the air, whilst carbonic oxide reduces the dried oxide at the ordinary temperatures with formation of silver and carbon dioxide.[2]

It decomposes soluble chlorides with formation of silver chloride, and precipitates the corresponding oxides from solutions of many metallic salts. When heated to 250° it begins to decompose, and it loses the whole of its oxygen at 300°. It is reduced by hydrogen at the ordinary temperature in the presence of a trace of water,[3] but large quantities of water retard this reaction. When rubbed in a mortar with antimony sulphide, arsenic sulphide, milk of sulphur, amorphous phosphorus, tannic acid, or other easily oxidisable substances, ignition takes place. It is dissolved by ammonia, the solution on exposure to air yielding fulminating silver, a black explosive compound which has the composition NAg_3 (p. 478)[4].

Silver oxide corresponds to the only well-defined series of silver salts, which may frequently be obtained from it by the action of the corresponding acid, but are usually formed by double decomposition, as most of them are insoluble in water, the principal exceptions being the nitrate and fluoride, which are readily soluble, and the sulphate and nitrite, which are sparingly soluble. The salts with colourless acids are usually colourless, but a few, such as the bromide, iodide, phosphate, and arsenate, are coloured. The soluble salts have a neutral reaction and unpleasant metallic taste, and are poisonous. Many silver salts, such as the sulphate and thiosulphate, are isomorphous with the corresponding salts of sodium and lithium.

Silver Peroxide, Ag_2O_2.—In 1804 Ritter obtained a black crystalline powder by passing an electric current between platinum electrodes through an aqueous solution of silver nitrate. This substance, which separated out at the anode in small octahedra, was found to give off oxygen when heated, and was for a long time considered to be silver peroxide.

[1] Levi, *Gazz.*, 1901, **31**, ii., 1.
[2] Dejust, *Compt rend.*, 1905, **140**, 1250.
[3] Kohlschütter, *Zeit. Electrochem.*, 1908, **14**, 49.
[4] See also Matignon, *Bull. Soc. chim.*, 1908, iv., **3**, 618.

Subsequent analyses,[1] however, have shown that it contains nitrogen and has the constant composition represented by the formula Ag_7NO_{11} or $3Ag_2O_2,AgNO_3,2O$, and the name of *silver peroxynitrate* is generally given to it. It has been pointed out, however, that when the assumption is made that the nitrate in the precipitate is present as silver nitrate, the results indicate that the oxide formed has the formula Ag_3O_4.[2] Black powders are also obtained by the electrolysis of solutions of other salts of silver; thus the sulphate yields *silver peroxysulphate*,[3] $5Ag_2O_2$, $2Ag_2SO_7$, whilst silver fluoride gives the *peroxyfluorides*,[4] $Ag_{15}F_3O_{16}$, and Ag_7FO_8.

Silver peroxide has also been obtained as a black precipitate by the action of potassium persulphate solution on silver nitrate or silver sulphate,[5] whilst it is stated to be formed when ozone acts on silver oxide and on silver (see p. 458).

The black substance, stated to be prepared by Wöhler by the electrolysis of dilute sulphuric acid using a silver anode, is probably not the peroxide, but the peroxysulphate.

Silver peroxide, as prepared from the peroxynitrate, is a grey powder of specific gravity 7·44 (Watson). It may be heated to 100° without decomposition, but at higher temperatures is decomposed into its elements, whilst when heated with dilute sulphuric acid it evolves half its oxygen, silver sulphate being formed. When treated with ammonia, nitrogen is liberated,[6] in an amount corresponding with the equation:

$$6Ag_2O_2+2NH_3=3Ag_4O_3+N_2+3H_2O.$$

The oxide Ag_4O_3 has, however, not yet been isolated.

Silver and the Halogens.

221 *Silver Subfluoride*, Ag_2F, is obtained as a bronze-like crystalline powder by heating a saturated solution of silver

[1] Mulder and Heringa, *Rec. trav. chim.*, 1896, **15**, 1 and 235; Mulder, *Rec. trav. chim.*, 1896, **16**, 57; 1903, **22**, 235 and 405; Šulc, *Zeit. anorg. Chem.*, 1896, **12**, 89 and 180; 1900, **24**, 305; Watson, *Journ. Chem. Soc.*, 1906, **89**, 578; Barbieri, *Atti. R. Accad. Lincei*, 1906, [v.], **15**, i., 500.

[2] Baborovsky and Kuzma, *Zeit. physikal. Chem.*, 1909, **67**, 48; see also *Zeit. Electrochemie*, 1908, **14**, 196.

[3] Mulder, *Proc. K. Akad. Wetensch. Amsterdam*, 1898; *Rec. trav. chim.*, 1900, **19**, 115.

[4] Tanatar, *Zeit. anorg. Chem.*, 1901, **28**, 331.

[5] Marshall, *Proc. Roy. Soc. Edin.*, 1900, **23**, 163; 1902, **24**, 88; *Journ. Chem. Soc.*, 1891, **59**, 771.

[6] Watson, *Journ. Chem. Soc.*, 1906, **89**, 578.

fluoride with metallic silver, and is reconverted into these by the addition of an excess of water.[1] According to Vanino and Sachs,[2] however, it is not a true compound, but a mixture of silver fluoride, silver, and silver oxide in varying proportions.

Silver Fluoride, AgF.—Hydrofluoric acid does not act upon metallic silver, but the fluoride is obtained by dissolving silver oxide or carbonate in aqueous hydrofluoric acid and evaporating to dryness. If the solution be allowed to evaporate in a vacuum, colourless, lustrous, deliquescent, tetragonal pyramids are deposited, having the composition AgF,H_2O (Marignac), whilst the concentrated solution when allowed to stand exposed to the air deposits hard transparent prisms of the compound $AgF,2H_2O$, which are nearly as deliquescent as calcium chloride. Under the influence of light, solutions of silver fluoride are decomposed with the formation of silver subfluoride and silver peroxide.[3] It is extremely difficult to obtain silver fluoride in the anhydrous state. The hydrate AgF,H_2O decomposes when dried in a vacuum, and yields a brown amorphous mass which still contains 1·5 per cent. of water, and dissolves in 0·85 part of water at 15°·5. When heated to the melting point of lead in a covered crucible, 0·5 per cent. less than the calculated quantity of water is given off, together with some hydrofluoric acid and oxygen:

$$4AgF + 2H_2O = 4Ag + 4HF + O_2.$$

This decomposition goes on until all the water is driven off and the salt melted, and from this point it can be heated in absence of air up to the melting point of silver without any further decomposition taking place.[4] The fused salt solidifies to a black mass which is elastic and may be cut with scissors. In the fused state it conducts electricity without being decomposed. The dry pulverulent salt absorbs 844 times its volume of ammonia.

It has been proposed to employ silver fluoride, under the name of tachyol, for the disinfection of drinking water.[5]

Silver Chloride, AgCl, occurs as the mineral *chlorargyrite* or *horn-silver*, which crystallises in octahedra and other forms of the regular system, but is more frequently found as a massive

[1] Guntz, *Compt. rend.*, 1890, **110**, 1337.
[2] *Zeit. anal. Chem.*, 1911, **50**, 623.
[3] Eisenreich, *Zeit. physikal. Chem.*, 1911, **76**, 643.
[4] Gore, *Phil. Trans.*, 1871, **161**, 321.
[5] Paternò and Cingolani, *Gazz.*, 1907, **37**, 1313.

wax-like mass, which generally has a pearl-grey colour, though sometimes it possesses a whitish and sometimes a violet-blue colour. It occurs at Andreasberg, mixed with alumina, as an earthy mass which is called butter-milk ore, and this ore was known to the older mineralogists. Gesner, in 1565, terms horn-silver *Argentum cornu pellucido simile*, and Matthesius, in his *Berg-Postilla*, published in 1585, terms it "glass-ore, transparent like horn in a lantern." The largest masses are brought from Peru, Chili, and Mexico, and the mineral also occurs in Cornwall, in Nevada, where it is abundant, in Arizona and other localities. The method of preparing silver chloride artificially was probably known to the old alchemists, but it is first distinctly mentioned in the works of "Basil Valentine," who says: "Common salt throws down ☽." This precipitate was afterwards termed *Lac argenti*, and when it was found that it was fusible, and solidified to a transparent horn-like mass, the name *Luna cornea*, first mentioned by Croll in 1608, was given to it. Libavius stated that the substance obtained by precipitating silver solution with common salt weighed less than the silver itself, but this statement was contradicted by Boyle; and Kunkel, in his *Laboratorium Chymicum*, speaking of this, says that many substances are difficult to separate from one another: "Such is seen in ☽ cornea, as 12 loth ☽ retain out of the common salt, 4 loth terra and salt." This determination is in fact nearly correct, for 12 parts of silver form 15·94 parts of silver chloride.

Silver chloride is formed, without the phenomenon of incandescence, when chlorine is passed over silver at a dull-red heat (Stas). It is also formed by the action of hydrochloric acid on the ignited metal, whilst on the other hand hydrogen is able to reduce silver chloride to the metal (Boussingault). Aqueous hydrochloric acid converts the surface of metallic silver into chloride of silver, and common salt solution acts in a similar way. Proust examined some piasters which had for many years lain at the bottom of the sea, and he found that the whole of the silver was converted into chloride. In order to prepare pure chloride of silver a solution of the nitrate is precipitated by hydrochloric acid or common salt; in this way a white curdy precipitate is obtained which, on standing, or more quickly on agitation, becomes powdery. This precipitate must be washed and dried in absence of light. It has a specific gravity of 5·5. On heating, silver chloride assumes a yellow colour and melts

at 460°, forming a dark-yellow liquid. This solidifies on cooling, forming a botryoidal, colourless, tough, solid mass which refracts light strongly, and is so soft as to take impressions of the nail.

Silver chloride and sodium chloride when melted together and cooled, form brittle, crystalline masses which are homogeneous[1]; the melting points vary from 460° (AgCl) to 792° (NaCl), showing that the salts form an unbroken series of mixed crystals.

Silver chloride volatilises at a white heat, the vapour density[2] agreeing approximately with the formula AgCl.

According to Stas,[3] fused chloride of silver is absolutely insoluble in water at the ordinary temperature, or at any rate its solubility does not reach the limit of our present tests for chlorine, which Stas places at 1 in 10,000,000. In boiling water, on the other hand, it is appreciably soluble.

The freshly precipitated curdy chloride is slightly soluble in cold water, but the solubility becomes less when the precipitate has become powdery by standing or shaking, measurements of the electrical conductivity showing that this form dissolves to the extent of 0·00152 grm.[4] at 18°, and 0·0218 grm.[5] at 100° in 1 litre of water. The solution becomes opalescent on the addition of either silver nitrate or hydrochloric acid. The presence of nitric acid does not affect the solubility of the curdy chloride, whereas the solubility of the powdery form increases proportionally to the amount of nitric acid added: 100,000 parts of concentrated nitric acid dissolve 2 parts of the freshly prepared silver chloride (Thorpe); on boiling, it is decomposed into nitrate with evolution of chlorine. One part of silver chloride dissolves in about 200 parts of concentrated hydrochloric acid, and in 600 parts of the acid diluted with an equal bulk of water. Soluble chlorides, such as sal-ammoniac and common salt, dissolve silver chloride tolerably easily, and it is very soluble in ammonia, 12·88 parts of aqueous ammonia of specific gravity 0·89 dissolving 1 part of silver chloride (Wallace and Lamont). It is likewise dissolved in quantity by mercuric nitrate, sodium thiosulphate, and potassium cyanide.

Various metals, such as iron and zinc, reduce the chloride to the state of metal in the presence of water, more rapidly in

[1] Botta, *Centr. Min.*, 1911, 138. [2] *Zeit. physikal. Chem.*, 1889, **4**, 267.
[3] *Compt. rend.*, 1871, **73**, 998.
[4] Kohlrausch and Rose, *Zeit. physikal. Chem.*, 1893, **12**, 242.
[5] Böttger, *Zeit. physikal. Chem.*, 1906, **56**, 83.

presence of hydrochloric acid and sulphuric acid. It is also decomposed by mercury when a solution of common salt is present. Cold sulphuric acid does not act upon it, but it is decomposed slowly, though completely, by the boiling acid with evolution of hydrochloric acid.[1] Concentrated hydriodic acid converts it with evolution of heat into silver iodide (Deville), and if moist, freshly precipitated chloride be treated with a solution of bromide of potassium, or iodide of potassium, it is completely converted into silver bromide or iodide.[2]

White silver chloride, obtained by precipitation, when exposed to light, is first coloured violet, then brownish-grey, and afterwards black. This alteration in colour was known to Boyle,[3] who, however, ascribed it to the action of the air. Scheele[4] afterwards proved that it was only discoloured on exposure to light, and he also showed that in this reaction hydrochloric acid was liberated and that on treating the residue with ammonia, black flakes of silver remained behind.

It has been shown by Abney and by Baker that the pure dry chloride does not blacken when exposed to light in a vacuous tube, in perfectly dry oxygen, or under pure carbon tetrachloride in the absence of oxygen. Baker[5] has also shown that not only is chlorine lost when the chloride blackens, but that oxygen is at the same time absorbed, an oxychloride of silver, Ag_2ClO, being probably formed. The amount of silver chloride which undergoes this change is, however, extremely small, even when a large quantity is exposed for a long period. The blackening is accelerated by the presence of substances which are capable of taking up chlorine, such as water, silver nitrate, stannous chloride, &c., and retarded by such as readily give up chlorine, such as chlorine water and ferric chloride. Some chemists still support the view that a sub-chloride of silver is produced.

Sonstadt[6] states that hydrogen peroxide is always formed when light acts on silver chloride. The same chemist finds that if silver chloride be sealed up in a tube and blackened by exposure to light, a reversion to white silver chloride takes place when the tube is kept in the dark: whereas if the products of decomposition of the choride by light are removed by sealing

[1] Sauer, *Zeit. anal. Chem.*, 1873, 376.
[2] Field, *Journ. Chem. Soc.*, 1858, 234. [3] *Op.* I., 756.
[4] *Von der Luft und dem Feuer*, Leipzig, 1784, p. 64.
[5] *Journ. Chem. Soc.*, 1892, **41**, 728. [6] *Proc. Chem. Soc.*, 1898, 371.

up calcium chloride and ammonia in another part of the tube containing the silver chloride, no bleaching of the blackened compound takes place in the dark.

Silver Chloride and Ammonia.—Glauber states that a calx is formed when silver solution is precipitated by common salt, and he adds that the calx "readily dissolves in *spiritu urinæ, salis armoniaci, cornu Cervi, succini, fuliginis et capillorum*, and may be used to form a good medicament." Faraday[1] first obtained a compound by the direct union of ammonia and silver chloride by saturating dry precipitated silver chloride with ammonia; 100 grains or 6·48 grams absorbed 130 cubic inches or 2·13 litres of the gas. The absorbed ammonia is again given off at 37°·7 (Faraday). When heated in a closed tube for the purpose of obtaining liquid ammonia, the compound fuses between 88° and 95°, swells up, and begins to boil at 99°, losing ammonia and gradually becoming white. Two compounds are formed by the direct union of ammonia with silver chloride; $AgCl,3NH_3$, which has a dissociation pressure of 618 mm. at 15°, and $2AgCl,3NH_3$, the dissociation pressure of which is 38·3 at the same temperature.[2]

When a solution of silver chloride in concentrated ammonia is rapidly evaporated, silver chloride crystallises out in glittering octahedra, but if it be allowed to evaporate at ordinary temperatures over quicklime, the compound $2AgCl,3NH_3$ separates out in colourless, birefractive prisms which are not affected by light.[3] On the other hand,[4] a solution of silver chloride in liquid ammonia, when evaporated at $-40°$ to $-20°$, deposits long colourless needles of the composition $AgCl,3NH_3$.

Bodländer and Fittig[5] have shown that solutions of silver chloride in ammonia contain the silver almost exclusively as the complex $Ag(NH_3)_2Cl$, although the solid in contact with the solution has the formula $2AgCl,3NH_3$.

Silver Bromide, AgBr, occurs in Chili and Mexico as the mineral bromargyrite, being usually found in small yellow or greenish masses, rarely crystalline. The mineral embolite is a mixture of silver chloride and bromide, varying from three of the latter to one of the former to the reverse proportion. It likewise occurs in Chili and Mexico, and is very similar to the

[1] *Quart. Journ. of Science*, 1818, **5**, 74.
[2] Horstmann, *Ber.*, 1876, **9**, 756.
[3] Jarry, *Ann. Chim. Phys.*, 1899 [4], **17**, 327.
[4] Jarry, *Compt. rend.*, 1897, **124**, 288.
[5] *Zeit. physikal. Chem.*, 1902, **39**, 597; see also Straub, *ibid.*, 1911, **77**, 331.

foregoing mineral. When an excess of silver nitrate is precipitated in the dark with hydrobromic acid, a white curdy precipitate is obtained which in contact with potassium bromide, or on heating, becomes yellow. It melts at 426°, and is soluble in a hot solution of hydrobromic acid, and in a solution of mercuric nitrate, separating out in octahedra from these solutions on cooling.

The solubility of silver bromide in water has been determined by measuring the electrical conductivity of the solution, and has been found to be 0·107 mgr. per litre at 21°,[1] and 3·7 mgr. at 100°.[2]

Silver bromide is scarcely soluble in dilute ammonia, but easily soluble in concentrated ammonia; it melts, on heating, to a reddish liquid which solidifies to a yellow lustrous mass, and the latter, when heated in a current of chlorine, is slowly converted into chloride. The finely divided precipitate suspended in water is instantly decomposed by chlorine, and hydrochloric acid gas also decomposes it at 700° with evolution of hydrogen bromide. It is soluble in sodium thiosulphate, the saturated solution corresponding to a double salt containing five molecules of silver bromide to nine molecules of crystallised thiosulphate. This salt exists only in solution, and on evaporation, or when precipitated with alcohol, yields

$$2Na_2S_2O_3,Ag_2S_2O_3,2H_2O.^3$$

Whilst the fused bromide is hardly acted upon by light, the precipitated salt is soon coloured a greyish-violet on exposure to light; if, however, it contains a trace of free bromine, it is unacted on. The action is also lessened by the presence of nitric acid, whilst it is increased by the presence of silver nitrate. Many chemists explain this darkening on exposure to light as being due to the formation of a sub-bromide, but it seems more probable that an oxybromide of silver is formed.

Stas[4] described several varieties of this salt which differ in their behaviour towards light.

Dry silver bromide absorbs no gaseous ammonia[5]; on the other hand, the ammoniacal solution deposits on standing white

[1] Kohlrausch and Dolezalek, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018.

[2] Böttger, *Zeit. physikal. Chem.*, 1906, **56**, 83.

[3] Lumière and Segewetz, *Bull. Soc. chim.*, 1907 [iv], **1**, 946.

[4] *Ann. Chim. Phys.*, 1874, (5), **3**, 289.

[5] Rammelsberg, *Pogg. Ann.*, 1842, **55**, 246.

glistening crystals, and these on heating lose ammonia,[1] whilst liquid ammonia below 4° converts silver bromide into a white substance, $AgBr,3NH_3$. This loses ammonia at 4°, yielding another white substance of the composition $2AgBr,3NH_3$, which gives off ammonia at 35°, silver bromide being left.[2]

Silver Iodide, AgI.—This salt occurs as iodargyrite in Mexico, Chili, Spain, and in the Cerro Colorado Mine in Arizona, in the form of slightly elastic hexagonal tablets. Silver combines directly with iodine on heating. The metal also dissolves in hydriodic acid, with violent evolution of hydrogen, and if the liquid be warmed as soon as the action becomes lessened, the evolution again increases, and, on cooling, colourless crystalline scales separate out. These on exposure to air decompose quickly, and probably possess the formula AgI,HI. The mother-liquor on standing deposits thick hexagonal prisms of silver iodide.[3] The same compound is formed by the action of concentrated hydriodic acid on silver chloride, and the iodide is also produced by the treatment of silver chloride or bromide with aqueous potassium iodide or other soluble iodides, silver iodide being deposited as a light yellowish powder. It is dimorphous and melts at 556°, forming a yellow liquid, which on further heating becomes red and then dark reddish-brown, and on cooling solidifies to a soft yellow mass having a specific gravity of 5·687 at 0° (Deville), whilst the crystalline variety has at 14° a specific gravity of 5·669, that of the precipitated salt being 5·596 (Damour). An interesting fact with reference to the abnormal expansion and contraction of silver iodide by heat has been observed by Fizeau[4]; it contracts when heated from −10° to +70°, and expands on cooling. This is explained by Rodwell,[5] by the fact that silver iodide exists in two modifications. Fizeau, however, determined the coefficient of expansion of three different varieties of silver iodide and found it to be negative in each case and G. Jones,[6] from a study of the free energy of formation of silver iodide, concluded that the affinity of the silver and iodine increases with rising temperature, which tends to cause a diminution in volume.

Measurements of the electrical conductivity of the solution

[1] Liebig, *Schweiggers Journ.*, **48**, 103. [2] Jarry, *Compt. rend.*, 1898, **126**, 1138.
[3] Deville, *Compt. rend.*, 1851, **32**, 894.
[4] *Compt. rend.*, 1867, **64**, 304. [5] *Chem. News*, 1875, **31**, 4.
[6] *J. Amer. Chem. Soc.*, 1909, **31**, 191.

show that silver iodide dissolves in water to the extent of 0·0035 mgr. in a litre.[1]

Pure silver iodide is left unaltered by the action of direct sunlight. If, however, it be precipitated from an excess of silver nitrate so that traces of this salt are carried down with it, it becomes coloured green on exposure to light, and in presence of more silver nitrate a deep greyish-black colour is attained although no loss of iodine is observed (Stas). Iodide of potassium, and nitric acid (specific gravity 1·2) have the power of reproducing the yellow colour. The changes effected by light upon silver iodide are brought about chiefly in the presence of substances which have the power of combining with a portion of the iodine. Ammonia changes the yellow colour of silver iodide to white and dissolves it very sparingly; it differs from the chloride and bromide of silver, inasmuch as it is only sparingly soluble even in concentrated ammonia, one part of the iodide dissolving, according to Wallace and Lamont, in 2493 parts of ammonia of specific gravity 0·89 ; its solubility in aqueous ammonia, however, increases appreciably with rise of temperature.[2]

It is readily soluble in liquid ammonia, and if the solution be allowed to evaporate at –40° to –10°, white crystals of AgI,NH_3 separate out.[3] This substance evolves ammonia at 4°, yielding the white compound $2AgI,NH_3$, which is also formed by the action of ammonia gas on dry precipitated silver iodide,[4] and which on exposure to air gives off its ammonia.

Silver iodide is tolerably soluble in a strong solution of potassium iodide, from which solution it is precipitated by the addition of water, whilst a hot solution of potassium iodide, saturated with silver iodide, deposits, on standing, white needles of a salt having the composition AgI,KI. When silver iodide is gently heated in chlorine gas it decomposes into silver chloride, and the same reaction takes place when it is treated with dry hydrogen chloride at 700° (Hautfeuille). It is only incompletely reduced in a current of hydrogen even when exposed to a white-heat (Vogel).

Silver Chlorite, $AgClO_2$, is obtained by precipitating a weak alkaline solution of a chlorite with silver nitrate. It forms

[1] Kohlrausch and Dolezalek, *Sitzungsber. K. Akad. Wiss. Berlin*, 1901, 1018.

[2] Baubigny, *Compt. rend.*, 1908, **146**, 1263.

[3] Jarry, *Ann. Chim. Phys.*, 1899, [7], **17**, 327.

[4] Rammelsberg, *Pogg. Ann.*, 1839, **48**, 170.

a crystalline substance which separates from a solution in hot water in crystalline scales. These deflagrate when moistened with concentrated hydrochloric acid, or when heated to 105°; they also take fire when mixed with sulphur (Millon).

Silver Chlorate, $AgClO_3$.—This salt is obtained when chlorine is passed into water through which silver oxide is diffused, until bubbles of oxygen are evolved; the chloride of silver is filtered off and the liquor evaporated to its crystallising point. Silver chloride and hypochlorite are first formed; part of the latter, according to Förster and Jorre,[1] is then hydrolysed to hypochlorous acid, and this reacts with the silver hypochlorite to form silver chlorate and chloride.

The chlorate may also be obtained by dissolving silver oxide in chloric acid, the action being accompanied with evolution of heat. It crystallises in white, opaque, tetragonal prisms, having a specific gravity of 4·43. These dissolve in about 10 parts of cold water, and melt at 230°; when further heated to 270°, they give off oxygen and a trace of chlorine. When mixed with sulphur it detonates with the utmost violence on friction.

Silver and Sulphur.

222 *Silver Sulphide*, Ag_2S, occurs as argentite, or vitreous silver. The occurrence of this ore was known to Agricola: "Argentum rude plumbei coloris et galenæ simile." This important silver ore, occurring in blackish-grey crystals, belonging to the regular system, occurs widely distributed, but is found especially in the Erzgebirge, in Hungary, in Norway near Kongsberg, in the Altai, in the Urals, in Cornwall, Bolivia, Peru, Chili, Mexico, and in Nevada, at the Comstock lode. This compound occurs in the Erzgebirge in two distinct forms; one of these is termed daleminzite, and the other acanthite; the first of these being isomorphous with chalcocite. Argentite can be obtained artificially, by igniting silver chloride in a current of sulphuretted hydrogen. Silver sulphide is also formed when silver is heated with sulphur or sulphuretted hydrogen, and forms the yellow or brownish stains which are formed on articles of silver on exposure to the air (Proust). Sulphuretted hydrogen produces in solutions of silver a blackish-brown flocculent precipitate of silver sulphide which is soluble in hot nitric acid, and is converted into silver chloride when a

[1] *J. pr. Chem.*, 1899, [2], **59**, 537; see also Vol. I., p. 350.

solution of copper chloride in the presence of common salt is added to it.

Silver Disulphide, Ag_2S_2, has been prepared by adding a solution of sulphur in carbon disulphide to a solution of silver nitrate in benzonitrile. It is a brown amorphous powder which oxidises very rapidly when moist, and is converted into silver sulphate by shaking with water and air. When heated in the air it melts to a red liquid and gives off sulphur and sulphur dioxide, metallic silver being left.[1]

Silver Sulphite, Ag_2SO_3, is a white curdy precipitate almost insoluble in water and sulphurous acid. It was supposed to decompose when heated to 100° into silver, silver sulphate, and sulphur dioxide, but Baubigny[2] has shown that only a small proportion is decomposed in this manner, more than 80 per cent. being converted into dithionate, thus:—

$$2Ag_2SO_3 = Ag_2S_2O_6 + 2Ag,$$

and that it is only at a much higher temperature that silver sulphate and sulphur dioxide are produced from the dithionate.

Normal Silver Sulphate, Ag_2SO_4.—This substance was obtained in solution by Glauber, for he states in his *De furnis novis philosophicis* (1648): "Dissolve *rasuram* ☽ in a rectified oil of vitriol, with the addition of a sufficiency of water, but not so much as in the case of Mars or Venus. Or, still better, dissolve a calx of ☽ which is precipitated from aqua fortis, either by copper or by spirits of salt."

It is best obtained by heating the reduced metal with sulphuric acid, or by dissolving the carbonate in dilute sulphuric acid. It forms small, lustrous rhombic crystals, which are anhydrous, and isomorphous with anhydrous sodium sulphate[3]; it has a specific gravity of 5·4, and dissolves to the extent of 0·77 parts at 17°, 1·46 parts at 100°, in 100 of water. In consequence of the sparing solubility of the salt, it is obtained as a precipitate when sulphuric acid or a soluble sulphate is added to a silver solution, and this fact was known to Boyle.[4] It is easily soluble in water containing sulphuric acid, and still more soluble in nitric acid, and also dissolves readily in strong sulphuric acid,

[1] Hantzsch, *Zeit. anorg. Chem.*, 1898, **19**, 104.

[2] *Compt. rend.*, 1909, **149**, 735, 858.

[3] Mitscherlich, *Pogg. Ann.*, 1827, **12**, 138.

[4] "Considerations and Experiments touching the origin of qualities and forms," Boyle, *Op.*, **3**, 66.

being precipitated from this solution on the addition of water. It fuses at a dark-red heat and decomposes at a very high temperature into metal, oxygen, and sulphur dioxide. When dissolved in less than three parts of sulphuric acid, light yellow prisms of *hydrogen silver sulphate*, $HAgSO_4$, are obtained.

According to Carey Lea,[1] a double salt of silver sulphate and a lower sulphate, having the formula Ag_4SO_4,Ag_2SO_4,H_2O, is obtained by the reduction of silver nitrate, phosphate or carbonate with hypophosphorous acid in presence of sulphuric acid; it forms a pale brown powder which is permanent in the air and does not evolve sulphuric acid even at a dull-red heat. It always contains about 2 per cent. of phosphoric anhydride, which cannot be removed even by treatment with strong sulphuric acid.

Silver Thiosulphate, $Ag_2S_2O_3$, is obtained by gradually adding a moderately dilute solution of silver nitrate to an excess of concentrated solution of sodium thiosulphate, washing the precipitated grey mixture of thiosulphate and sulphide with cold water, extracting the thiosulphate with ammonia, precipitating it as quickly as possible by exact neutralisation with nitric acid, and quickly drying it by pressure between filter paper.[2] It forms a snow-white powder, having a sweet taste; it is slightly soluble in water, and in the moist condition it easily decomposes into sulphuric acid and sulphide of silver (Rose):

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

Silver Sodium Thiosulphate, $AgNaS_2O_3$, was discovered by Herschel, and may be obtained by evaporating a solution of silver chloride in aqueous sodium thiosulphate, until it crystallises. It is, however, best prepared by adding a neutral solution of silver nitrate to a solution of sodium thiosulphate, until a permanent precipitate is produced. The solution is then filtered and alcohol added, when the salt is precipitated in silky laminæ (Lenz). Its solution, evaporated in a vacuum, deposits tabular crystals of the salt. It is soluble in water and possesses a sweet taste (Herschel). A saturated solution of silver chloride in sodium thiosulphate corresponds to the formula $2Na_2S_2O_3,Ag_2S_2O_3,2H_2O$, and this solution deposits a salt corresponding to the formula $Na_2S_2O_3,Ag_2S_2O_3,2H_2O$.[3] A

[1] *Amer. J. Sci.*, 1892 (3), **44**, 322.

[2] Herschel, *Edin. Phil. Journ.*, 1819, **1**, 26; **2**, 154.

[3] Lumière and Segewetz, *Bull. Soc. chim.*, 1907, [iv], **1**, 946.

number of double thiosulphates of silver and potassium are also known.[1]

Silver and the Elements of the Nitrogen Group.

223 *Silver Nitride,* NAg_3.—This compound, usually known as Berthollet's fulminating silver, was first obtained by the above-named chemist in 1788, by the action of ammonia on the silver oxide prepared by precipitating a silver solution with lime water. It is a black powder which, especially in the dry state, explodes most violently on the slightest percussion, or even on touching with a feather. Great care is necessary in working with ammoniacal solutions of silver oxide and such solutions should not be kept.[2] Raschig [3] has shown that the compound has the composition NAg_3, but it is usually mixed with a certain quantity of metallic silver. In some cases the powder was also found to contain hydrogen, and had then the formulæ $NHAg_2$. A yellow nitride of silver is stated to be formed when magnesium nitride and silver nitrate are gently heated together in a sealed tube. It is decomposed by water with formation of silver oxide and ammonia.[4]

Silver Amide, $AgNH_2$, is formed as a white precipitate when a solution of potassamide in liquid ammonia is added to excess of silver nitrate dissolved in the same solvent. It is soluble in solutions of ammonium salts in liquid ammonia, darkens on exposure to light, and when dry readily explodes.[5]

Silver Azoimide, AgN_3, is obtained by the addition of silver nitrate to a solution of azoimide or one of its soluble salts. It forms minute prisms, which are insoluble in water and readily explode with extreme violence.

Silver Hyponitrite, $Ag_2N_2O_2$, is a yellow precipitate which is deposited from ammonia in small yellow crystals.[6] It is sparingly soluble in water, and when moist is slowly decomposed at ordinary temperatures. When pure it does not explode when heated, but decomposes into nitrogen, oxides of nitrogen, silver nitrate, and silver.[7]

[1] Rosenheim and Steinhäuser, *Zeit. anorg. Chem.*, 1900, **25**, 72.

[2] See Matignon, *Bull Soc. chim.*, 1908, [iv], **3**, 618; also Sieverts, *Zeit. angew. Chem.*, 1909, **22**, 6.

[3] *Annalen*, 1886, **233**, 93.

[4] Smits, *Rec. trav. chim.*, 1896, **15**, 135.

[5] Franklin, *J. Amer. Chem. Soc.*, 1903, **27**, 820.

[6] Krischner, *Zeit. anorg. Chem.*, 1898, **16**, 424.

[7] Divers, *Journ. Chem. Soc.*, 1899, **75**, 95.

Silver Nitrite, $AgNO_2$.—This substance was first obtained by Proust, who regarded it as the nitrate of silver suboxide, having obtained it by boiling a solution of silver nitrate with the powdered metal. It is best prepared by mixing lukewarm solutions of 24 parts of silver nitrate and 15 parts of potassium nitrite. On cooling, silver nitrite separates as a white crystalline powder, which may be readily filtered. It is less soluble in cold water than silver sulphate, but dissolves more readily in hot water with partial decomposition. When slowly deposited it forms long, acicular, rhombic crystals.

When heated, silver nitrite decomposes without fusion at 180°,[1] according to the following equations:—$AgNO_2 = Ag + NO_2$; $Ag + 2NO_2 = AgNO_3 + NO$; $AgNO_2 + NO_2 = AgNO_3 + NO$.

Silver Nitrate, $AgNO_3$.—This salt was obtained in the crystalline form by Geber: "Dissolve ☽ calcinatam in aqua dissolutiva, quo facto, eoque eam in phyala, cum longe collo, non obturato ori per diem solum, usque quo consumetur ad ejus tertiam partem aquæ, quo peracto pone in loco frigido, et devenient lapilli ad modum crystalli fusibiles." At the end of the seventeenth century, Angelus Sala drew the attention of the iatro-chemists to this salt, known as *crystalli dianæ* or *magisterium argenti*, to which, when cast into sticks, the name of *lapis infernalis* or *lunar caustic* was given.

Fig. 119.

Silver nitrate is obtained on the large scale, by dissolving silver in dilute nitric acid, and occurs in commerce both in crystals and cast into sticks (lunar caustic). It crystallises in transparent rhombic plates (Fig. 119), having a specific gravity of 4·328 (Schröder) and melting at 209°, solidifying on cooling to a white, fibrous, crystalline mass. It is dimorphous, passing into a hexagonal modification at 159°.[2] It possesses an acrid, metallic taste, and acts as a violent poison, blackening and destroying organic matter, but it does not blacken in the air except in contact with organic substances. When it is wrapped up in paper for some time it gradually decomposes, leaving a residue of metallic

[1] Divers, *Proc. Chem. Soc.*, 1905, 281; see also Oswald, *Compt. rend.*, 1911, **152**, 381.

[2] Compare Guinchant, *Compt. rend.*, 1909, **149**, 569.

silver, and at a red heat it yields nitrogen peroxide, oxygen, and metallic silver.[1]

100 parts of water dissolve as follows[2]:

At	0°	20°	50°	80°	100°	110°	
$AgNO_3$	115	215	400	650	910	1110	parts.

The aqueous solution has a neutral reaction. If ammonia be added to a solution of silver nitrate until the precipitate first formed redissolves, and this solution be then allowed to evaporate, fine bright rhombic prismatic crystals, having the composition $AgNO_3,2NH_3$, are deposited. These do not give off ammonia at 100°, but when more strongly heated they melt, evolving nitrogen and ammonia, whilst ammonium nitrate and a metallic mirror of silver are left behind. When a current of dry ammonia is passed over dry silver nitrate, this substance absorbs 29·55 per cent. of the gas, enough heat being developed to produce fusion of the mass. The product of this reaction is a white solid soluble in water and possessing the formula $AgNO_3,3NH_3$ (Rose).

Silver nitrate is largely used in chemical analysis and especially in photography. It is also employed in medicine both externally and internally. For external application it acts as a powerful cautery, inasmuch as it unites with the albuminoid substances to form insoluble compounds. Large doses given internally act corrosively upon the mucous membrane, producing serious inflammation. Experiments on animals have shown that it produces paralysis of the nerve centres, difficulty of breathing, and coma. It is given in doses of from 0·02 gram in chronic stomach diseases, epilepsy and other nervous affections. When administered for some length of time, it produces a peculiar bronze colour of the skin, caused by the deposition of metallic silver under the cuticle.

224 *Silver Biphosphide*, AgP_2, may be prepared by passing phosphorus vapour over finely divided silver or silver chloride heated at 400°. The product must be cooled in an atmosphere of phosphorus vapour, as it decomposes at the temperature of formation when heated in an inert gas.[3]

[1] Divers, *Journ. Chem. Soc.*, 1899, **75**, 83.

[2] Kremers, *Pogg. Ann.*, 1854, **92**, 497; see also Étard, *Ann. Chim. Phys.*, 1894, (7), **2**, 526; Meyerhoffer, *Landolt-Börnstein Physikalisch-Chemische Tabellen* (Berlin, Springer, 1905), 520.

[3] Granger, *Compt. rend.*, 1897, **124**, 896; *Chem. News*, 1898, **77**, 227.

Phosphates of Silver.—The *normal phosphate*, Ag_3PO_4, is formed as a yellow precipitate, when a silver salt is added to a solution of any one of the sodium orthophosphates. On heating, its colour changes to brown, and it melts at a red heat. It is soluble in aqueous phosphoric acid, yielding the *mono-hydrogen salt*, HAg_2PO_4, which is deposited in the form of white crystals. The *pyrophosphate*, $Ag_4P_2O_7$, is a white compound, melting below a redheat to form a dark-brown liquid which solidifies to a colourless fibrous mass. When heated for some time with aqueous phosphoric acid, the *dihydrogen pyrophosphate*, $H_2Ag_2P_2O_7$, is formed as a crystalline powder, which is decomposed by the addition of water. The same compound may also be formed by heating silver pyrophosphate with pyrophosphoric acid until a clear fused mass is obtained, dissolving the cooled product in a small quantity of water at 0°, and adding alcohol, when it is precipitated as a white crystalline powder melting at 240°.[1] The *metaphosphates of silver* are white compounds.

Arsenites and Arsenates of Silver.—The *normal arsenite*, Ag_3AsO_3, is a canary-yellow powder, easily soluble in nitric acid and ammonia. When the ammoniacal solution is boiled, metallic silver separates out. The *normal arsenate*, Ag_3AsO_4, is a dark red-brown crystalline powder, formed by precipitating a concentrated solution of arsenic acid with a boiling solution of silver nitrate. The same substance is precipitated as a brownish-red powder if a solution of an arsenate be added to silver nitrate.

Silver Acetylide or Silver Carbide, C_2Ag_2.—When acetylene is passed into aqueous silver nitrate a white precipitate is first formed consisting of the compound $C_2Ag_2,AgNO_3$, which with more acetylene changes to white silver acetylide. It may also be obtained by passing acetylene into ammoniacal silver nitrate.[2]

Silver Carbonate, Ag_2CO_3, is a light-yellow powder of a paler colour than the phosphate, which readily becomes black on exposure to light, or on heating, and loses all its carbon dioxide at 200°. When a mixture of ammonio-nitrate of silver and caustic potash is exposed to the air, silver oxide separates out, and after a time lemon-yellow needles of the carbonate.

When silver nitrate is added to a concentrated solution of potassium carbonate a yellow precipitate separates out, and

[1] Cavalier, *Compt. rend.*, 1904, **139**, 284.

[2] Arth, *Compt. rend.*, 1897, **124**, 1534; Chavastelon, *ibid.*, 1564.

this quickly changes to the white compound *silver potassium carbonate*, $AgKCO_3$.[1]

Silver Cyanide, AgCN, is a white curdy precipitate, easily soluble in ammonia. On heating with water or with caustic potash solution it is reduced to metallic silver.[2] It is insoluble in cold dilute nitric acid, but dissolves in the hot acid, forming silver nitrate and hydrocyanic acid, which may be removed by distillation.[3] It forms soluble double salts with the cyanides of the metals of the alkalis, and alkaline earths.

Potassium Silver Cyanide, $KAg(CN)_2$, crystallises in feathery tufts or six-sided prisms, and is soluble in 4 parts of water at 20°.[4] It does not undergo alteration on exposure to light.

Silver Cyanamide, Ag_2CN_2, may be obtained by precipitating an alkaline solution of sodium cyanamide with silver nitrate. On heating, it explodes more or less violently, the gases formed by the explosion being cyanogen and nitrogen.[5]

Silver Cyanate, AgCNO, is a white precipitate easily soluble in ammonia and nitric acid. On heating it explodes, a dull white mass of silver carbide remaining behind. This decomposes, on solution in nitric acid, leaving a finely-divided network of pure carbon.[6]

Silver Thiocyanate, AgCNS, is a white curdy precipitate, easily soluble in ammonia, and crystallising from the solution in glistening scales which do not contain any ammonia.

Potassium Silver Thiocyanate, $KAg(SCN)_2$, is formed when the foregoing salt is dissolved in a solution of potassium thiocyanate. It forms monoclinic crystals, melts at 140°, and is decomposed by water.

Photography.

225 The observation of Boyle, that silver chloride and other silver salts undergo blackening on exposure to light, the chemical explanation of which was first given by Scheele, has led to the foundation of the important art of photography. The first light-pictures were obtained by Thomas Wedgwood, in the year 1802. These were simply prints of leaves or paintings on glass

[1] Reynolds, *Journ. Chem. Soc.*, 1898, **73**, 265.
[2] Marsh and Struthers, *Proc. Chem. Soc.*, 1903, 249.
[3] Plimmer, *Journ. Chem. Soc.*, 1904, **85**, 12.
[4] Baup, *Ann. Chim. Phys.*, 1858, [3], **53**, 462.
[5] Ellis, *Chem. News*, 1909, **100**, 154.
[6] Liebig and Redtenbacher, *Annalen*, 1841, **38**, 129.

prepared by allowing the light to fall through a more or less transparent object on to white paper or leather, which had been moistened with nitrate of silver. Davy, repeating these experiments, obtained fairly accurate copies of leaves, wings of insects, and similar objects, and even succeeded in preparing pictures of small objects, which had been magnified by the solar microscope. The pictures thus obtained could not be exposed to daylight, but had to be examined by candle-light, as at that time no process was known by which that portion of the silver salt unacted upon by the light could be withdrawn, and the picture thus rendered permanent. The first experiments which aimed at rendering the photographic image permanent were made by Niépce, who began his investigations in the year 1814. In 1826 he, together with Daguerre, investigated the same subject, and it is to the latter experimenter that we are indebted for the first process by which the image obtained in the camera can be fixed. In 1839 he discovered the process which now bears his name. This consists in allowing the vapour of iodine to act upon a polished surface of silver, which thus becomes coated with a film of silver iodide. The surface of the plate thus prepared is next exposed to light in the camera. After a short time the light has produced its action, although on the removal of the plate no change of the surface is perceptible. If the plate be now exposed to the action of the vapour of mercury, the picture makes its appearance, inasmuch as the mercury is deposited in extremely fine globules on those portions of the plate on which the light has fallen, whilst in the shadows, the unaltered iodide remains. In order to remove those portions of the iodide which had been unacted upon by the light, Daguerre at first used a hot solution of common salt, but Herschel at once pointed out the advantages of sodium thiosulphate for this purpose, and it was immediately adopted by Daguerre.[1]

The Daguerreotype process underwent many alterations, but it has now been altogether superseded by much more convenient methods. In the year 1839 Fox Talbot published his method of photogenic drawing, or photography on paper. This process, which was but an imperfect one, consisted in exposing in the camera a paper soaked in a weak solution of common salt and afterwards washed over with a solution of silver nitrate. The image obtained was a negative one; that is, the light portions of the landscape were dark, and *vice versâ*.

[1] Eder, *Geschichte der Photographie*, pp. 203, 209 (Knapp, Halle a.S. 1905).

These pictures were fixed by immersion in a solution of common salt. A great improvement was made in this process by Talbot in the year 1841, by coating the paper which was to be acted upon with a film of silver iodide by first dipping it into a solution of silver nitrate and then into one of potassium iodide. This paper does not exhibit any change after exposure in the camera, but on "development" with a mixture of silver nitrate, acetic acid and gallic acid, the image becomes visible. The picture is a negative, but it may be rendered transparent by saturating it with white wax, and then a positive print may be prepared from it by placing it on a paper moistened with chloride of silver, and exposing it to sunlight. This method was long known as the Talbotype or Calotype process.

A most important improvement in photography was made by Archer (1851), in the employment of a transparent film of iodised collodion spread upon glass as a sensitive film for the camera in place of the iodised paper used in the Talbotype process. Collodion is a solution of pyroxylin, consisting of the lower nitrates of cellulose, in a mixture of alcohol and ether, and to this is added a certain proportion of a soluble iodide or bromide, usually of zinc or cadmium. On pouring the solution on to the plate the ether and alcohol evaporate, and the plate becomes covered with a homogeneous film. The collodionised plate is next dipped into a bath of silver nitrate, and the plate thus "sensitised" is exposed, still wet with the silver nitrate solution, in the camera. The image produced on the film is in this case also latent, and requires to be developed or made visible by treating the surface with reducing agents, such as ferrous sulphate or pyrogallic acid, compounds which have the power of reducing it to the condition of metallic silver. The unaltered iodide may be removed by dissolving it in cyanide of potassium or sodium thiosulphate, and from the negative thus obtained any number of positive prints can be prepared, each of which is afterwards fixed in sodium thiosulphate. The application of collodion renders the process much more certain, shortens the necessary exposure to a few seconds, and admits of a far greater degree of precision in the reproduction of detail than was possible on the rougher surface of paper in the Talbotype.

Many attempts were made to lessen the inconvenience attaching to wet plate photography by washing the plate free from silver nitrate, covering it with a film of some substance such as tannin, albumin, &c., and then drying.

All these plates are, however, much surpassed in sensitiveness towards light by the modern dry plate, which consists of a glass plate coated with an emulsion in gelatin of silver bromide, sometimes accompanied by a little iodide. This emulsion is made by adding ammoniacal silver nitrate to a solution of an excess of potassium bromide and gelatin in hot water. The mixture is then heated at 45° for some time, a process termed "ripening," until the emulsion attains its most sensitive condition. During this operation a physical change appears to occur, the particles of bromide, which when first precipitated have a diameter of 0·0008–0·0015 mm., increasing during the process to 0·003–0·004 mm. in diameter. The emulsion is then washed, to remove the potassium bromide and nitrate, placed on the plate in a uniform film and dried. When such a plate is exposed to light a latent image is produced which can be developed by many reducing agents which do not attack unexposed silver bromide. The reducing agents employed as developers include ferrous oxalate, which passes during the process into ferric oxalate, pyrogallic acid (tri-hydroxybenzene), hydroquinone (quinol, *para*-dihydroxybenzene) and metol (*para*-methylamino-phenol); in presence of an alkali such as ammonia or potassium carbonate, these hydroxy-compounds are converted by oxidation into quinones and similar substances. In order to prevent too vigorous development and consequent fogging of the plate, a *restrainer* or *retarder*, consisting of the bromide of the alkali used, is added to the developer.[1] The plates are then "fixed" by washing with sodium thiosulphate solution, which dissolves out the silver bromide unacted on by the developer, leaving the silver image.

The exact change in the sensitive salt that is effected by the light is not yet understood, the chief fact known being that the developer removes the bromine from the silver bromide where the light has fallen upon the film, whilst it is unable to bring about this change in those parts of the film where the light has not preceded it. If an exposed plate be treated with a halogen element or an oxidising agent such as nitric acid, potassium dichromate, &c., it is found that the image can no longer be developed.

Several theories have been advanced as to the nature of this change, all of which may be classed into two groups; the one attributing it to a chemical and the other to a physical change

[1] See Lüppo-Cramer, *Zeit. Chem. Ind. Kolloide*, 1909, **4**, 92, and Sheppard, *ibid.*, 1909, **5**, 43.

in the silver bromide. According to the first of these views, the light causes a very small amount of bromine to be lost by the silver bromide, a sub-bromide being formed. This bromine is taken up by the gelatin, which thus acts as a sensitiser and replaces the silver nitrate of the wet collodion plate and the tannin of the dry collodion plate. Many hold that the sub-bromide thus formed has the composition Ag_2Br, whilst Eder,[1] from the alteration in the action of certain reagents on plates exposed to light for varying periods, concludes that several sub-bromides are obtained depending on the length of the exposure. Another view is that an oxybromide of silver is formed with loss of bromine, and not a sub-bromide. During development the altered silver bromide is first reduced and the reducing action becomes extended to the silver bromide in the immediate proximity of this reduced silver. It will be seen that according to this theory the density of the silver image which can be obtained by development is limited only by the thickness of the film, the amount of silver produced increasing steadily with the duration of the development. It has, however, been shown by Hurter and Driffield [2] that the maximum density attainable depends entirely on the length of the exposure and the intensity of the light, and is not altered by prolonging the development beyond a certain necessary time. The same chemists have further proved that when a plate is exposed so long that the whole of its silver bromide can be reduced to metallic silver by development, no evidence of the formation of hydrobromic acid, which would accompany the action of bromine on gelatin, can be detected, and that the whole of the bromine in the plate is given up to the developing liquid.

It has, moreover, been found by Dewar that gelatin emulsions of silver bromide remain sensitive to light, although to a somewhat smaller extent, even at a temperature of −252·5° C., at which nearly all chemical reactions proceed extremely slowly.

These results, therefore, have given rise to the view that no chemical decomposition is brought about by the light, but that the silver bromide molecule undergoes a physical alteration which renders it capable of being reduced by the developer.

[1] Eder, Address to the Viennese Academy of Sciences, *British Journ. Phot.*, 1905, **52**, 950 and 968; see also Trivelli, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **11**, 730.

[2] *J. Soc. Chem. Ind.*, 1890, **9**, 455; Sheppard and Mees, *Proc. Roy. Soc.*, 1905, **74**, 44.

Joly,[1] who supports the physical hypothesis, considers that the light causes an electronisation of the silver bromide.

It is well known, from the experiments of Hertz and others, that light has the power of discharging negative electrification from the surface of many bodies; that is, of bringing about the escape of negatively charged electrons (p. 40); and such bodies are termed "photo-electric." It has also been found that the halogen salts of silver are vigorously photo-electric, and possess an activity in the descending order, bromide, chloride, and iodide, which is the same order as their photographic sensitiveness.

Moreover, an image capable of development is also formed by the action of cathode rays, or the electronic discharge from radium. Joly, therefore, considers that the latent image is made up of atoms or molecules electronised by the action of light on the silver halide salt, and that it is upon these that the developer acts. A number of experiments, in which the rate of action of developers upon the silver bromide of exposed plates was measured, have been carried out by Sheppard and Mees,[2] and their results point to the conclusion that the reducing agent in the development acts upon ionised silver bromide with formation of metallic silver.

H. Weitz [3] considers the latent image to consist of a solid solution of silver sub-halide and possibly silver in silver halide, but Lüppo-Cramer [4] considers that the assumption of the formation of sub-chloride or sub-bromide is unnecessary and that the latent image is a colloidal compound. He also explains the peculiarities of the silver deposits obtained with different developers, and with gelatin and collodion films, by the more or less colloidal nature of the silver and by adsorption of different substances from the developers.[5]

The question cannot, however, as yet be considered as settled.

226 *Action of Light of Different Degrees of Refrangibility on the Salts of Silver.*—Scheele observed that the violet rays of the solar spectrum are those which affect silver chloride most strongly, and to these the name of chemical rays has frequently been given. It has, however, been shown that all the rays of the solar spectrum are able, under certain circumstances, to

[1] Address to the Photographic Convention of the United Kingdom, Dublin, 1905; *British Journ. Phot.*, 1905, **52**, 551.

[2] *Proc. Roy. Soc.*, 1905, **74**, 447; 1905, **76**, A, 226; 1907, **78**, A, 461.

[3] *Zeit. physikal. Chem.*, 1906, **54**, 305.

[4] *Zeit. Chem. Ind. Kolloide*, 1907, **2**, 135. [5] *Ibid.*, 1908, **3**, 33, 135.

effect chemical change, each particular chemical compound being decomposed by the rays upon which it is most capable of exerting an absorbent action. Not only is this the case, but an addition to the sensitive compound of certain coloured, but chemically inactive, substances has the effect of altering the position of the maximum of chemical action for that particular compound. Thus, for example, it is possible by the addition of a yellowish-red colouring matter, such as aurin, to the bromide film to prepare a plate which is more affected by the yellow rays than the untreated plate, whilst the addition of erythrosin confers increased sensitiveness to the yellow and orange rays, and of cyanin to the red rays.

These dyes cause the bromide film with which they are mixed to be specially sensitive to the rays corresponding roughly to their absorption spectra. In this way Draper,[1] Vogel,[2] and Abney[3] have succeeded in photographing the lines of the visible solar spectrum from *b* downwards, and have not only secured pictures of the portions included between the lines *E* and *A*, but have obtained photographic action even in the infra-red regions. Orthochromatic plates are now made by means of which the relative intensity of the various colours to the eye is much more truly represented.[4] The exact function of the dyes in producing this effect is not understood, but they are known to be photo-electric, and it has been suggested by Joly that the electron-producing power for that particular ray absorbed by the dye is responsible for the special sensitiveness it produces in the film.

For a full account of the theory and practice of photography, the reader is referred to Abney's "Instruction in Photography," Chapman Jones's "Science and Practice of Photography," and to Meldola's "Chemistry of Photography."

Detection and Estimation of Silver.

227 There is probably no element whose presence can be more readily detected by chemical methods than silver, owing to its chloride being insoluble in water and easily soluble in ammonia. In order to detect silver in an insoluble compound, it may be melted with sodium carbonate on charcoal

[1] *Phil. Mag.*, 1877, [5], **3**, 86. [2] *Ann. Phys. Chem.*, 1885, **26**, 527.
[3] *Phil. Mag.*, 1878, [5], **5**, 61.
[4] *See* Bothamley, *Brit. Assoc. Rep.*, 1895, 661.

before the blowpipe or simply heated on charcoal in the reducing flame of the blowpipe. Silver is then obtained in the metallic state as a bright shining bead, which easily dissolves in warm nitric acid, the solution giving on the addition of hydrochloric acid a curdy precipitate of silver chloride, or, if only a trace of silver be present, a mere opalescence. This disappears on the addition of ammonia, but is reproduced when the ammonia is neutralised with nitric acid.

The spark spectrum of silver is obtained by the use of poles of the metal with a powerful discharge. It may also be seen when platinum poles are moistened with silver nitrate solution. Two bright green lines are the most characteristic in its spectrum, and several weaker lines occur in both the blue and the violet.

Silver is estimated gravimetrically as the chloride. The precipitate after washing and drying is heated in a porcelain crucible until it begins to melt, and then its weight is obtained. In some few cases the silver is determined as the cyanide or sulphide, and, in the case of organic silver salts, the metal which remains behind on heating the salt is weighed.

Silver can also be easily determined volumetrically with standard hydrochloric acid, common salt solution, or potassium thiocyanate. In the mints, where a large number of silver assays has to be made daily, a method proposed by Gay Lussac [1] is often adopted. In this process the alloy is dissolved in nitric acid, and the silver precipitated from solution in the form of chloride, the volume of the standard solution necessary for the complete precipitation of the silver being ascertained. Chemically pure silver is required for standardisation; this is best used in the form of thin foil; then a standard solution of common salt is needed of such a strength that 100 c.c. correspond exactly to one gram of silver; thirdly a salt solution 1-10th of this strength, prepared by diluting one volume of the standard solution to ten volumes.

Sufficient of the alloy (of which the composition must be known approximately) to contain a little more than one gram of silver is accurately weighed, placed in a bottle, and dissolved in nitric acid. One hundred c.c. of the standard solution of salt are then added and the bottle well shaken. The titration is then continued with the 1-10th strength solution until precipitation

[1] *Instruct. sur l'Essai des Matières d'Argent par la Voie Humide.* Paris, 1833.

is complete. Each c.c. of standard solution corresponds to 0·01 gram, and each c.c. of the second solution to 0·001 gram of silver.

Another method of assaying silver still used, although not so accurate as the method just described, is the assaying of silver by cupellation. This process depends on the fact that the metals alloyed with silver oxidise in the presence of lead oxide at a high temperature, yielding an oxide which, together with the oxide of lead, is absorbed by the porous cupel, whilst any silver which the mixture contains is left behind in a bright globule which can be accurately weighed. The assay is usually made with 0·25 to 0·5 gram of silver. The process of assaying by cupellation, even in experienced hands, may vary as much as two parts in 1,000, whilst Gay Lussac's process admits of an accuracy of 0·5 in 1,000. The process of cupellation is, however, still in use in lead works, where it is required to determine the amount of silver which marketable lead contains, and it is also used for the estimation of silver in ores.

The electrolytic method has also been used for the determination of silver, a solution of the nitrate being used, and alcohol or potassium cyanide added to prevent the formation of the black compound described on page 465.[1]

The atomic weight of silver was determined with considerable accuracy by Stas, by the methods described on p. 13, the average of the numbers obtained by the different methods being 107·93.

Guye and Ter Gazarian[2] have found that potassium chlorate crystallises with a small quantity of chloride as an impurity, the amount being nearly constant, about 2·7 parts in the thousand. Applying this correction to Stas's ratios, the atomic weight of silver is lowered from 107·93 to 107·89. The number now adopted (1913) is 107·88.

GOLD (AURUM). Au = 197·2.

228 Of all the metals gold was probably the first to attract the attention of man, its occurrence in the native state, its brilliant lustre, and its permanence, rendering it an object of value from very early times.

[1] Küster and von Steinwehr, *Zeit. Elektrochem.*, 1898, **4**, 451; Wolman, *ibid.*, 1897, **3**, 537.

[2] *Compt. rend.*, 1906, **143**, 411; see also Richards and Wells, *J. Amer. Chem. Soc.*, 1905, **27**, 459.

Metallic gold is mentioned in the Old Testament and in Homer, and the various names by which it is designated denote lustre or fine colour. Thus in the Hebrew *zahâb*, the root signifies to glitter; whilst the Greek word χρυσός, probably derived from the Sanscrit *hiranya*, also signifies to glitter or flame. Our word "gold" probably is connected with *jvalita*, which also occurs in Sanscrit and is derived from *jval*, which means to shine. As being the most perfect of the metals gold was compared by the alchemists to the sun: to it were attributed the most singular virtues, and strenuous efforts were directed to the transmutation of the baser metals into ☉ (Sol).[1]

Gold is usually found in the native state, but never perfectly pure, being always alloyed with more or less silver. Native gold sometimes also contains small quantities of copper, and traces of iron, bismuth, platinum, palladium, or rhodium. Gold is likewise found in the following compounds: bismuth-aurite, Au_2Bi; calaverite, $AuTe_2$; sylvanite or graphic tellurium, $(Au,Ag)Te_4$; nagyagite or foliated tellurium, $(Pb,Au)_2(Te,S,Sb)_3$; white tellurium, $(Au,Ag,Pb)(Te,Sb)_3$. Small quantities of gold occur in many pyrites, blendes, and other ores. It has also been found in sea water.[2]

Native gold is generally found *in situ* in quartz veins or reefs which intersect metamorphic rocks, and to some extent also in the wall-rock of these veins. Metamorphic rocks which are thus intersected are generally chloritic, talcose, and argillaceous schists; also, though less commonly, mica- and hornblende-schists; gneiss, diorite, and porphyry, and, still more rarely, granite. Gold is frequently found crystalline, the commonest forms being the octahedron and tetrahedron. The crystals are, however, sometimes acicular, through elongation of these two forms, passing into filiform, reticulated, and arborescent shapes, and occasionally exhibiting a spongy form from the aggregration of filaments. It frequently occurs in masses termed nuggets, also in thin laminæ, and often in flattened grains or scales and in rolled masses in sand or gravel. Sometimes indeed it is so finely disseminated throughout the quartz that it is not visible, though present in quantities sufficient to pay for its extraction.

[1] Those interested in the processes employed by the alchemists in the search after the philosopher's stone are referred to Thomson's *History of Chemistry*, and Berthelot, *Collection des Anciens Alchimistes Grecs*, and *La Chimie au Moyen Âge* (Paris, 1887–1893).

[2] Liversidge, *Trans. Roy. Soc., N.S. W.*, 1896.

The occurrence of gold is not confined to the above-named rocks, the metal being found in many formations, even up to the chalk.

The sands, gravels, and clays formed by the disintegration of the gold-bearing rocks form an important source of the precious metal, and these alluvial deposits often occur of considerable thickness and of great extent.

The relative amount of gold present both in the quartz veins and the alluvial deposits is extremely small, varying from one part in 70,000 in the quartz to one in 1–15 millions in alluvium.

229 Although gold occurs widely distributed in nature it is only found in certain places in quantities sufficient to repay the expenses of extraction. The most important European localities are Russia, Hungary, and Germany. Gold is also found in the Alps, but the mines there, which were worked from the times of the ancients, are now altogether abandoned or worked but very slightly.

Gold has also been found in Cornwall, and the precious metal is now being worked to a small extent in Wales. Gold has also been found in Scotland, especially near Leadhills, and in Glencoich and other parts of Perthshire, in Ireland in County Wicklow, in Sweden, and in Spain, where mines were worked by the Romans. In Asia, gold occurs chiefly on the eastern flanks of the Urals and in other parts of Siberia, but the metal has been found in almost all parts of this continent, especially in India, Japan, China, Korea, Borneo, and the Dutch East Indies. The vessels of gold in the possession of the ancient Scythians, which according to Herodotus were said to have fallen from the skies, were probably made from Uralian gold. The mines in the Urals were, however, not opened until the year 1819, but they soon became of such importance that they supplied the greater portion of the world's requirements until the discovery of Californian gold.

Africa also contains much gold. Thus a considerable quantity of gold dust has been found in Abyssinia, also on the coast opposite Madagascar, supposed by some to be the *Ophir* of Solomon, and in various parts of the interior of the western portion of the continent whence it was formerly sent to the Gold Coast. Indeed this source, together with that of Hungary and the Brazils, yielded the chief supply of gold up to the beginning of last century. West Africa has a considerable gold-mining industry. Since the year 1884, the gold-fields of the Transvaal have become of great importance, the

output having risen almost continuously since that date. In 1895 the amount of gold obtained from the Rand district was 2,549,036 ozs., whilst in 1905 it had increased to 4,897,221 ozs., and in 1911 to 8,237,700 ozs., surpassing the output from any other country.

In the year 1849 gold was discovered in California by Colonel Sutter, who having erected a saw-mill noticed that the water which was used to work the mill contained particles of gold. The attempt to keep this discovery secret naturally failed, and the few hundred inhabitants of the city of San Francisco rushed to the gold-diggings, and were soon followed by emigrants from all parts of the world. For the first few years Californian gold was obtained entirely from alluvial washings, but since 1852 true gold-mining has been on the increase. Considerable gold-fields exist in the western portion of the North American continent, reaching from Mexico up to British Columbia and the Klondyke district.

Australia is another country rich in gold-fields. Important gold-mines occur in the table-lands of New South Wales and along the continuation of the Australian cordillera in Victoria, in Queensland and Western Australia, whilst smaller supplies are drawn from South Australia and Tasmania.

It is a matter of general notoriety that many years before anything was published respecting the existence of gold in Australia, gold was often brought into Sydney by shepherds and settlers in the bush. The actual occurrence of gold in Australia was, however, first discovered by Count Strzelecki in the year 1839, but this was not made known at the time, inasmuch as the Governor feared the consequences of such a statement in the existing conditions of the colony. In 1843–4 Count Strzelecki returned to England and exhibited his nuggets and gold specimens to Sir Roderick Murchison, who, arguing from the comparison of these with samples from the gold-bearing Urals, predicted that gold would be found widely distributed in the eastern chains of the Australian mountains. In the years 1841–3 gold was also found by the Rev. W. D. Clarke, an Australian geologist. To Mr. Hargreaves, an old Californian gold-digger, however, belongs the honour of proving, in 1851, that gold existed in large quantities in various parts of the colony, and of showing how it could be readily obtained from alluvial deposits by means of the cradle. The first discovery of workable gold-fields was made at Ophir, and this soon led to the finding of the precious metal in the soil and rocks of the

colony over tracks many miles in extent. After a short time the proclaimed gold-fields extended, with a few intervals, the whole length of the colony, and westward about 200 miles, comprising an area of about 1,356 square miles, and numbering more than eighty distinct fields.[1]

Gold has also been found in New Zealand and New Caledonia. The Australian is, as a rule, much purer than the Californian gold, but it is a singular fact that the average fineness of the gold found in the several Australian colonies shows a regular depreciation as we advance northwards. Thus the average fineness of Victorian gold is about 960 ; that of the New South Wales gold is 935, while still further north in Queensland the average fineness is 872, and Maryborough gold contains only 85 per cent. of gold and as much as 14 per cent. of silver.[2] Very large nuggets occur in Australian fields ; thus, for instance, one found at Ballarat weighed 184 pounds and was valued at £8,376 10*s.* 6*d.*

The total production of gold reached a very high mark in the fifties when the Australian discoveries followed on the opening of the Californian fields. During these years the annual production averaged £30,000,000, but afterwards gradually fell off, until in the period 1880–90 it averaged only about £20,000,000.

Since that date it has constantly increased with the exception of the years 1900–1902, when the production was affected seriously by the Boer War. This increase is chiefly due to the large output from Africa consequent upon the development of the Transvaal fields, but also because of the improved methods employed for the extraction of the metal.

The following figures give the production in ounces of fine gold from each of the great gold producing countries for the years 1895, 1905, and 1910.[3]

	1895.	1905.	1910.
Australasia	2,070,335	4,159,220	3,160,605
United States	2,261,612	4,260,504	4,657,017
Russia	1,537,584	1,063,883	1,716,722
Transvaal	1,811,391	4,897,221	7,526,860
Rest of Africa	257,806	580,620	891,708
India	218,186	576,889	546,862
Canada	92,448	700,863	493,751
Mexico	270,924	702,799	1,093,053
Other Countries	1,203,325	1,489,071	1,847,906
Total	9,723,612	18,431,070	21,934,484

[1] Liversidge, *Trans. Roy. Soc., N.S.W.*, ix., 153.

[2] Miller, *Trans. Roy. Soc., N.S.W.*, 1870.

[3] *Mineral Industry*, 1897, 6, 260 ; 1905, 14, 236 ; 1911, 20, 283.

Composition of Native Gold.—The following table gives the composition of several kinds of native gold.

Locality.	Barbara (Siebenbürgen).	Katharinenberg (Ural).	Senegal.	Bolivia.	California.	Australia.	Transvaal.
Analyst.	Rose.	Rose.	Levol.	Forbes.	Hunt.	Northcote.	Cohen.
Gold . .	84·80	93·34	94·40	94·73	89·24	99·28	94·48
Silver . .	14·68	6·28	5·85	5·23	10·76	0·44	5·16
Iron . . .	0·13	0·32	—	0·04	—	0·20	Trace
Copper .	0·04	0·06	—	—	—	0·07	0·25
Platinum .	—	—	0·15	—	—	—	—
Bismuth .	—	—	—	—	—	0·01	—
	99·65	100·00	100·40	100·00	100·00	100·00	99·89

230 *Gold Extraction.*—The simplest method of extracting gold, namely, *alluvial-washing* or *placer digging*, as it is termed in California, carried on from the simple pan-washing to hydraulic mining on a stupendous scale, necessarily requires a considerable quantity of running water. This or a similar process was in use amongst the ancients; thus Pliny describes the "bringing of rivers from the mountains, in many instances for a hundred miles, for washing the débris," &c., &c.

The washing apparatus is simple enough, though frequently ingenious. The simplest of all these operations is that termed *pan-washing*, in which a shallow pan is used, of iron or zinc, sinking into a cavity in the middle in which the heavy particles collect, whilst the lighter dirt is washed away. The wash-dirt or wash-stuff is brought into the pan in a stream of running water and the mass well stirred up with the hand so that the larger stones and heavy particles are left whilst the mud flows over the edge of the pan. The gold, which is found when the stones are picked out, is usually mixed with magnetic sand; it is dried and then brought into a shallow dish, and the black sand separated by blowing, the whole being kept in a state of constant rotation.

The *cradle* is another simple apparatus for gold-washing, much used in the early days of the gold discoveries in California and Australia. It consists of a trough or cradle of wood or iron six or seven feet in length under which rockers are placed, so arranged that the cradle has a slanting position to allow the mud

and water to run off. At the top of the cradle is a grating or sieve upon which the wash-stuff is thrown, and transverse bars of wood are placed across the bottom of the cradle to arrest the passage of the heavier particles of gold. Four men are needed to work this efficiently; one digs out the auriferous wash-stuff, another brings it to the cradle, a third rocks the trough, and the fourth attends to the proper supply of water and the uniform washing of the material.

Other forms of apparatus used for washing gold-bearing deposits are the long tom and the sluice. The *long tom* consists of an inclined trough about 12 feet long, the lower end of which is closed by a screen inclined at an angle of about 45°. Below this screen is placed the upper end of a riffle-box, consisting of another trough 12 feet long fitted with riffles which are sometimes supplied with mercury. The gravel is shovelled into the upper trough and a stream of water is allowed to play upon it, washing down the fine gravel and gold into the riffle-box where the coarse gold is caught on the riffles.

The *sluice* consists of a number of boxes, hundreds sometimes being used, each resembling the upper box of the long tom; they are about 12 feet long and 4 inches wider at one end than at the other, the narrow end of each box fitting into the wide end of that next below it. Riffle boxes are placed at certain intervals in these boxes to intercept all heavy particles that pass down, such as gold, mercury, amalgam, pyrites, &c. The usual grade of the boxes varies from 8 inches to 20 inches in 12 feet, depending on the fall of the ground, on the nature of the material to be washed and on the amount of water available. A certain amount of mercury is added in sluicing to aid in the collection of the gold.

231 *Hydraulicing.*—This method of working is largely used in California and New Zealand. It consists in breaking down the auriferous gravel by the impact of powerful jets of water and allowing the disintegrated material to pass along a series of sluices. To carry out this process successfully, an immense amount of water is necessary under a good pressure, a head of from 100 to 300 feet generally being used. The nozzles for the discharge of the water vary in size up to 11 inches in diameter, and require special appliances to control them. The sluices used are similar to those described above, but are larger and made altogether stronger. A quantity of mercury is generally used to amalgamate and help to collect the gold.

232 *Extraction of Gold from Quartz, &c.*—The general method for the extraction of the Gold from quartz consists in crushing the ore first to a moderate size in a rock-breaker, and then to a much finer state (usually with water) in a stamp battery.[1]

A *stamp battery* (Fig. 120) consists of a number of stamps, which are heavy pestles made of iron or steel weighing from 400 to 1,750 lbs. each ; these are raised by means of cams, keyed to a horizontal shaft, coming in contact with tappets fixed on to the upper portion of the stems, and are allowed to fall by their own weight. These stamps work in mortars made of

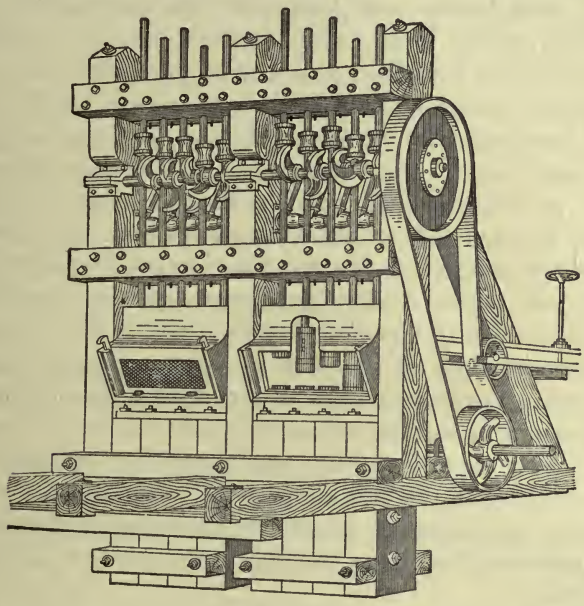


Fig. 120.

cast iron and weighing from $1\frac{1}{2}$ to 3 tons; as a general rule five stamps work in each mortar. Mercury is often placed inside the mortar, and the upper portions and sides of the latter are lined with amalgamated copper-plates. The pulp is discharged through screens of varying sizes according to the nature of the material under treatment, and then passes over a series of amalgamated plates, the tailing being generally treated by the cyanide process for the extraction of the remaining gold.

[1] Frequently ball mills and rolls are used instead of the stamp battery, especially in those cases in which the ore is crushed dry. Ball mills are not suitable, however, for wet crushing or for extremely hard ores.

Very often the tailings from stamp batteries contain a certain proportion of heavy minerals, such as iron pyrites, copper pyrites, galena, &c., and as these contain gold which is not collected on the amalgamated plates, they are extracted in some form of concentrating machine and are called concentrates. When these consist of copper pyrites or galena they are treated by smelting, but when they consist of iron pyrites they are treated by Plattner's chlorine process or by the cyanide process. The gold amalgam is scraped off the plates at certain intervals by means of rubber pads, cleaned, strained through wash-leather, and heated in iron retorts, the porous gold which remains being melted and cast into iron moulds.

Many methods have been proposed for promoting the amalgamation of the gold contained in the crushed ore, but the use of various materials for this purpose was much more general in the past than at the present time. The chief substance used is potassium cyanide, which, in the form of a dilute solution, is supposed to assist amalgamation; its action is probably a cleansing one, keeping the mercury free from grease and oil, and thus rendering it more active. Sodium is also used to clean the mercury before applying it to the plates. It is essential that all traces of grease be removed from the plates before amalgamation, and for this purpose a solution of caustic soda or sodium carbonate is used.

The losses of gold during amalgamation may be due to insufficient care on the part of the men, to the use of a method of working unsuitable to the ore, to the presence of float-gold, to the presence of injurious minerals in the ore, or to improperly kept plates.[1]

233 *Gold Extraction by Chlorine.*—For the purpose of extracting gold from auriferous pyrites Plattner's chlorine method is sometimes employed. In this process the pyrites is roasted, in order to remove the sulphur and arsenic and to render the ore porous, then moistened with water, and placed in tubs furnished with false bottoms, beneath which chlorine is introduced. After all the air has been replaced by chlorine, and the whole mass has become impregnated with this gas, the tubs are allowed to stand for about twenty-four hours, and the soluble gold chloride washed out with water.

In some cases the chlorination is carried out in revolving

[1] Full information concerning the metallurgy of gold may be found in *The Metallurgy of Gold* by Rose (Griffin & Co.), 1902.

lead-lined steel barrels or cylinders, the chlorine being produced by the action of sulphuric acid on bleaching powder placed inside the barrel. In this way a pressure of about two atmospheres is produced, and a charge of $3\frac{1}{2}$ tons is chlorinated in an hour and a half. The gold chloride solution is filtered through an asbestos cloth placed inside the barrel and passes directly into the precipitation tank. The metal may be precipitated from the solution by a number of different substances, the chief of which are ferrous sulphate, sulphuretted hydrogen, solid charcoal and sulphide of iron or copper; the reaction being as follows in the case of ferrous sulphate:

$$AuCl_3 + 3FeSO_4 = Au + FeCl_3 + Fe_2(SO_4)_3.$$

Sulphuretted hydrogen and metallic sulphides precipitate a sulphide of the metal, whilst charcoal precipitates the metal. The precipitate is collected, dried, roasted if it consist of the sulphide, and the metal then fused with borax.[1]

At Mount Morgan a modification of the chlorination process is employed in which the crushed ore is leached with chlorine water, the gold being precipitated from solution by means of charcoal.

It has also been proposed to employ bromine for the extraction of gold, either as bromine water or by liberating nascent bromine by the action of sulphuric acid on a mixture of bromide and bromate of sodium or calcium.

234 *The MacArthur-Forrest Cyanide Process.*—Finely-divided gold dissolves readily in a weak solution of potassium cyanide in the presence of atmospheric oxygen, a soluble double cyanide being formed:

$$4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH.$$

This reaction is now employed on a very large scale for the extraction of gold from the tailings obtained from the stamp batteries, which only contain a small amount of metal, and from such ores as are not readily treated by amalgamation. The process consists of four operations, viz.: the preparation of the ore; treatment with solution of potassium cyanide; precipitation of the gold; and treatment of the precipitated gold.

In many cases the tailings from the stamp batteries only need sizing in order to be ready for the process, and this sizing consists of the separation of slimes or very finely-

[1] *J. Soc. Chem. Ind.*, 1896, **15**, 336.

divided ore from the sandy portions, as these slimes tend to resist the percolation of the cyanide solutions. In the case of low grade ores which are treated direct by the cyanide process these are crushed down by rock-breakers and rolls, care being taken to prevent the formation of slimes.

For the treatment with cyanide solution, large vats are used, made of wood, iron, or cement, and holding from 10 to 600 tons of material. These vats are provided with false bottoms which usually consist of frameworks of wood pierced with holes and covered by canvas or cocoanut matting, below this being placed a layer of coarse sand and pebbles. The vats are filled to within a few inches of the top and levelled.

It is often found advisable before treating with the cyanide solution to give a preliminary wash with water to remove soluble salts, or to use a solution of soda or lime to neutralise acids due to the decomposition of pyrites in the ore. In the Transvaal the material is first treated with a solution of cyanide containing about 0·3 per cent. of KCN, which is allowed to percolate for a period varying from 6 to 24 hours according to the richness and nature of the ore; then a further treatment with a weak solution containing 0·05 to 0·15 per cent. is made, lasting from 24 to 48 hours. The amount of liquid used is generally about half a ton for every ton of ore. After the treatment with cyanide is finished, that is, when no more gold is being dissolved, the solution is drawn off as completely as possible, and the charge thoroughly washed with water and discharged. The tanks are emptied usually through doors in the bottom, either by hand labour or by sluicing out by means of water under pressure.

During the last few years large quantities of unleached slimes from previous working have been treated successfully at a very low cost by agitation in large tanks with cyanide solution for the extraction of the gold. After agitation the slimes are allowed to settle and the gold-bearing cyanide solution is drawn off, or else the slimes are pumped into large filter presses which separate the solution, leaving the solid matter in the form of cakes.

Fine grinding of the whole of the ore to pass through a 150 or 200 mesh sieve (40,000 holes to the square inch) in tube-mills, or grinding in pans after partially pulverising in the stamp battery, followed by agitation and filter-pressing in pressure- or vacuum-filters of the later types, of which there are a number

of successful forms on the market, has become the practice recently adopted on many of the great mines. In some cases of refractory ores, roasting is found necessary before cyanide treatment.

For the precipitation of the gold, the cyanide solutions from the tanks are passed through wooden troughs divided by baffle boards into a series of compartments containing freshly-turned zinc shavings which effect the precipitation of the gold:

$$2KAu(CN)_2 + Zn = 2KCN,Zn(CN)_2 + 2Au.$$

A zinc-lead couple is found to be more effective for the precipitation of gold from solutions containing copper and from very weak cyanide solutions, and for this purpose the zinc shavings are pickled in a 10 per cent. solution of lead acetate until covered with a black coating. The gold-bearing cyanide solutions are sometimes agitated with zinc dust and the residues filter-pressed.

The precipitated gold, together with any silver in the ore, is separated as far as possible from the zinc, and then may be treated, after roasting, by smelting with suitable fluxes, such as sand, borax, and sodium bicarbonate. Plumbago crucibles are generally used for these charges, and the resulting bullion may be 800 fine, *i.e.* contain 800 parts of gold per 1,000.

Another method for treating the precipitated gold is to dissolve out the zinc with dilute sulphuric acid and then to wash and dry the insoluble residue and smelt down with suitable fluxes; this generally gives a bullion from 850 to 900 fine.

A more recent process, which is said to effect a saving in cost and to be attended by less loss of gold, is Tavener's lead-smelting method, in which the precipitate is melted with litharge, assay slags and sawdust in a reverberatory furnace for the production of a lead bullion containing about 10 per cent. of gold which is afterwards cupelled.

In the Siemens-Halske process, the gold is deposited from solution by means of an electric current. The anodes are made of iron and the cathodes on which gold is deposited are of lead. These sheets of lead are afterwards melted down and cupelled for the extraction of the gold.

235 *Refining and Parting of Gold.*—The gold bullion obtained by the above processes varies very considerably in composition according to its origin and the treatment to which it has been subjected. It usually contains a considerable amount of silver

along with copper, iron, lead, antimony, and other base metals. When the amount of these is at all considerable it is usual to submit the bullion to a preliminary refining process before removing the silver. This is done by melting the metal in a crucible with borax and nitre, the base metals being thus oxidised and removed by skimming.

The parting of silver from gold was formerly carried out by means of nitric acid, this process having been first employed, it would appear, at Venice in the fifteenth century, for extracting the gold from Spanish silver. It remained in general use up to the beginning of last century, and is still frequently employed. It depends on the fact that nitric acid removes practically all the silver from an alloy of gold and silver, provided that a sufficient excess of silver be present. It was at first thought that the limiting proportion was 1 of gold to 3 of silver, and hence the process was termed *inquartation*, but it has been found that the method succeeds even when as much as 1 of gold is present to 2 of silver; the proportion most generally used is 1 of gold to $2\frac{1}{3}$ or $2\frac{1}{2}$ of silver.

For this process the bullion is first made up to the 'parting' proportion, and then granulated. The granules are boiled for 5 or 6 hours in nitric acid of specific gravity 1·2, the gold is then allowed to settle and the supernatant liquor siphoned off. A second boiling for 2 to 3 hours, and a third for 1 or 2 hours follow, with nitric acid of specific gravity 1·4. The gold residue is then well washed with water, pressed and melted down; whilst the silver in solution is precipitated by means of common salt and reduced to metallic silver by means of zinc.

Parting by Sulphuric Acid.—In 1753 Scheele discovered that sulphuric acid could be employed for this purpose. In a memoir on the subject, read before the Stockholm Academy, he says: "Sulphuric acid also dissolves silver when no water is amongst it, but gold is not in the least degree altered, so that silver and gold can be thus completely separated from one another; but such an oil of vitriol is much dearer than nitric acid, and for this reason it is not advisable to use it for this purpose, as there are other acids which cost less." Hence it was only when sulphuric acid became cheaper that the process of separation by its means could be carried out, and this was done by Darcet in 1802.

In order to separate the two metals by this method the alloy must not contain more than 33 per cent. of gold. If it be richer than this, it must be first melted with the necessary quantity of

silver. The granulated alloy is heated in cast-iron boilers, together with two and a half times its weight of concentrated sulphuric acid of specific gravity 1·85. Each vessel is covered with a dome of lead, and the sulphur dioxide which is evolved during the solution of the silver is either allowed to escape into the air, or is led into sulphuric acid chambers. As soon as no further evolution of this gas takes place, sulphuric acid, of specific gravity 1·69, is added for the purpose of dissolving the copper vitriol. The clear liquid is then allowed to flow into leaden pans containing the mother-liquors of copper vitriol formed in the next operation, and the whole is heated by steam in order to keep the slightly soluble silver sulphate in solution. Here a further quantity of gold is deposited, the clear liquid is again drawn off, and the silver precipitated by means of metallic copper. The finely-divided gold is again treated with sulphuric acid in order to render it completely free from silver, and after having been well boiled, it is washed and fused in a plumbago crucible with sodium bicarbonate.

In a modified form of the process the sulphuric acid solution of the silver is diluted with steam, and the silver sulphate allowed to crystallise out. The crystals are then removed and reduced by heating in a furnace with charcoal.

Parting by Chlorine.—When gold does not contain more than 10 per cent. of silver, it may be purified by Miller's process with chlorine gas, first introduced by him in the Sydney Mint. This process consists in melting the gold in a clay crucible which has been glazed inside with borax, and passing chlorine gas through the molten metal by means of a clay pipe. The chlorine at once combines with the silver to form silver chloride, which rises to the surface of the molten metal, whilst the chlorides of zinc, bismuth, antimony, and arsenic, should these metals be present, are volatilised, and the pure gold remains beneath. A layer of melted borax is placed on the top of the fused mass in order to prevent the silver chloride which is formed from being volatilised. The fineness of the gold thus prepared varies from 991 to 997 in 1,000 parts, whilst the metal obtained by other refining processes frequently contains a larger quantity of silver. This method of treatment may also be adopted with advantage for refining and toughening gold which is rendered brittle by the presence of small quantities of antimony, bismuth, tin, arsenic, &c.[1]

Electrolytic Refining and Parting of Gold.—For this purpose

[1] Roberts-Austen, *First Annual Report of the Mint*, 1870, 95.

the Wohlwill process is used, which in its latest form [1] uses a combination of a direct and an alternating current, as by this means it is found that the difficulties presented when the amount of silver in the bullion exceeds 50 parts per 1,000 are somewhat overcome. The electrolyte contains from 2 to 5 per cent. of hydrochloric acid, and from 2·5 to 6 per cent. of gold chloride.

Refining Gold Bullion with Oxygen Gas.—Rose [2] has shown that impure bullion and zinc precipitates from the cyanide process may be refined and toughened by blowing a stream of oxygen or air through the molten metal contained in a crucible and covered with a slag, made by the addition of borax and silica to the crucible charge. The metals are oxidised in succession, each in turn partially protecting those which are less easily oxidised than itself.

236 *Preparation of Pure Gold.*—In order to prepare gold containing less than one part of impurity in 10,000, gold cornets are dissolved in aqua regia, the liquid evaporated down, and traces of platinum removed by the addition of potassium chloride and alcohol. The clear solution of gold chloride is then allowed to stand, decanted from any precipitated chloride of silver, and reduced by warming with oxalic acid. The precipitate is repeatedly washed with hydrochloric acid, water, and ammonia, and is then fused in a clay crucible with potassium bisulphate and borax.

237 *Properties.*—Gold is distinguished from all the other metallic elements by its bright yellow colour. It crystallises in the regular system, and in the native state is often found in distinct though small crystals. Some Australian gold worth about £1,100 consisted of grains from the size of a large pea to that of small grains of sand, all of which were more or less perfect dodecahedra.[3] Native gold has also been found crystallised in a very great variety of other forms of the regular system.[4] These small crystals are frequently connected together, so as to form hair-like filaments termed *moss-gold.* Liversidge [5] has obtained this form of gold artificially. He noticed the occurrence

[1] *Met. and Chem. Eng.*, 1910, **8**, 82.

[2] *Trans. Inst. Min. and Met.*, 1904–1905, 377.

[3] Dana, *System of Mineralogy*, 5 Ed. p. 8; see also Liversidge, *Journ. Chem. Soc.*, 1897, **71**, 1125.

[4] von Rath, *Zeit. Kryst. Min.*, 1877, **1**, 1.

[5] *Proc. Roy. Soc., N. S. Wales*, 1876, 125.

of crystallised gold in certain specimens of Australian auriferous pyrites, and he therefore roasted this mineral in a muffle, for the purpose of removing arsenic and sulphur, but at a temperature insufficient to bring about the fusion either of the mineral or of the gold. On removing the sample from the muffle, small cauliflower-like excrescences of metallic gold were observed on the surface of the mass, these excrescences being composed of fine filaments of the metal often wound round in spiral coils. This form of gold has also been obtained by Moissan [1] by distillation of gold in the electric furnace.

Gold precipitated from a concentrated solution by ferrous sulphate forms very small cubes, and that obtained by reduction with oxalic acid consists of minute octahedra, which are usually much distorted, whilst both forms are obtained when solutions of auric chloride or bromide are reduced with formaldehyde in the presence of nitric or hydrochloric acid.[2]

When an amalgam containing 5 per cent. of gold is heated for eight days to 80°, and then treated with hot nitric acid, an aggregate of crystals, some of which are 6 mm. in length, may be obtained. These, after heating to get rid of the mercury, have a bright lustrous appearance.

Gold is softer than silver, and is the most ductile of metals. This was known to Pliny, who says: "Superque omnia netur, ac texitur lanæ modo." [3]

Although the relation which the Roman weights and measures bear to those in use in the present day is still somewhat uncertain, the following statement may be of interest as showing the progress of the art of gold-beating. In the first place we read in Pliny, "nec aliud laxius dilatatur, aut numerosius dividitur, utpote cujus unciæ in septingenas et quinquagenas, pluresque bratteas, quat ernum utroque digitorum spargantur." [4] Then in 1621 Mersenne mentions that the Paris gold-beaters were in the habit of obtaining 1,600 leaves from one ounce of gold, which would cover 105 square feet. In 1680 Halley states that in his time a grain of gold could be drawn into a wire 98 ells in length, whilst Reaumur mentions in 1711 that one ounce of gold can be hammered out so as to cover 146½

[1] *Compt. rend.*, 1905, **14**, 977.

[2] Awerkieff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 828.

[3] *N.H.*, **33**, 19.

[4] *N.H.*, **33**, 19. An ounce of gold can be hammered into 750 leaves, each of which is 4 digits (about 3 inches) square.

square feet, and according to newer statements one grain may be made to cover 56·75 square inches, or one ounce to cover 189 square feet, whilst 280,000 leaves have to be placed one upon another to occupy the thickness of one inch. One grain of gold also serves to gild two miles of fine silver wire, whilst the thickness of such deposits of gold as, for example, that on gold lace is about 0·000002 mm. Gold is extremely ductile, and gold wire can be drawn so fine that 3,240 metres of it weigh only one gram. Gold leaf has usually a thickness of about 0·0001 mm., and allows green light to pass through it.

The relations of finely-divided gold to light have been carefully examined by Faraday.[1] By spreading a leaf of gold on a glass plate and then pouring on to it a solution of potassium cyanide, Faraday succeeded in obtaining films of gold of extreme tenuity. The green colour which ordinary gold leaf exhibits by transmitted light passes into a ruby-red when the highly attenuated film is heated to 316°. At 550°, gold leaf becomes apparently transparent,[2] due to the aggregation of the gold leaving spaces through which light passes, the metal itself becoming opaque. The red colour of ruby glass is due to the presence of metallic gold in an extreme state of division.[3] This is also the case with the above-mentioned film, the original green tint of which can be brought back by burnishing its surface.

The specific gravity of crystalline gold obtained by reduction of auric chloride [4] is 19·431 at 20°, whilst gold distilled in vacuo was found to have the specific gravity 18·884 at 20°/4°, which increased to 19·2685 when the metal was submitted to a pressure of 10,000 atmospheres.[5] It melts at 1064°, expanding considerably in the act of fusion and forming a bluish-green liquid. Gold loses weight perceptibly on heating even at temperatures only 100° above its melting point;[6] it may be distilled in the electric furnace, and condenses in yellow leaflets, in moss-like filaments, or in yellow cubes.[7]

Gold has the specific heat 0·0324; it is exceeded in conductivity for heat and electricity only by silver and copper, its

[1] *Phil. Trans.*, 1857, **147**, 145.
[2] Turner, *Roy. Soc. Proc.*, 1908, A. **81**, 301.
[3] Zsigmondy, "Zur Erkenntnis der Kolloide," Jena, 1905.
[4] Awerkieff, *Zeit. anorg. Chem.*, 1903, **35**, 329.
[5] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.
[6] Rose, *Journ. Chem. Soc.*, 1893, **63**, 714.
[7] Moissan, *Compt. rend.*, 1905, **141**, 977.

electrical conductivity being 76·7 per cent. and its thermal conductivity 53·2 per cent. of that of silver.

Gold is not attacked at any temperature either by oxygen or by water, and it also remains unacted upon when fused with potassium chlorate. Alkalis and the nitrates, however, attack it. Gold does not dissolve in any single acid, with the exception of selenic (Mitscherlich), but it dissolves readily in aqua regia, or in any acid liquid in which chlorine, bromine, or iodine [1] is evolved, and in solutions of the easily decomposable perhalogen compounds of the metals, such as $FeBr_3$, $CoCl_3$, &c.

238 *Colloidal Gold.*—Solutions of colloidal gold, which are either red, purple, blue, or green, have been prepared in a number of ways. Red and blue solutions of colloidal gold were prepared by Faraday by reducing gold chloride by means of phosphorus. Bredig [2] obtained reddish-purple and blue solutions by passing an electric arc under water between gold wires (see p. 73); these solutions decomposed hydrogen peroxide, whilst freezing or the addition of electrolytes caused the separation of metallic gold. When aluminium foil is placed in an aqueous solution of auric chloride, colloidal gold is formed after some hours.[3] If aluminium chloride be added to the auric chloride solution, however, the gold is simply replaced by the aluminium, no colloidal gold being formed.[4] Colloidal gold has also been prepared by warming solutions of auric chloride with sodium lysalbate or protalbate,[5] formaldehyde, hydrazine hydrate, sugar solution, and other reducing agents,[6] and also by the action of the mould *aspergillus oryzæ* on very dilute solutions of this salt.[7]

The different colours of colloidal gold solutions are due to differences in the forms of the particles.[8] Distinct forms exist

[1] Nickles, *Ann. Chim. Phys.*, 1867, (4), **10**, 318.

[2] *Zeit. angew. Chem.*, 1898, 951.

[3] Carnot, *Compt. rend.*, 1883, **97**, 105, 169.

[4] Dauve, *J. Pharm. Chim.*, 1909, [vi.], **29**, 241.

[5] Paal, *Ber.*, 1902, **35**, 2236.

[6] Zsigmondy, *Annalen*, 1898, **301**, 29; Küspert, *Ber.*, 1902, **35**, 4070; Gutbier, *Zeit. anorg. Chem.*, 1902, **31**, 448; 1902, **32**, 347; 1904, **39**, 112; Henrich, *Ber.*, 1903, **36**, 609; Garbowski, *ibid.*, 1903, **36**, 1215; Hanriot, *Compt. rend.*, 1904, **138**, 1044; Vanino and Hartl., *Ber.*, 1905, **38**, 463; 1906, **39**, 1696; Donau, *Monatsh.*, 1905, **26**, 525; Vanino, *Zeit. Chem. Ind. Kolloide*, 1907, **2**, 51. See also *An Introduction to the Physics and Chemistry of Colloids*, Emil Hatschek. (J. and A. Churchill).

[7] Vanino and Hartl, *Ber.*, 1904, **37**, 3620.

[8] Steubing, *Ann. Physik.*, 1908, [iv.], **26**, 329.

for the red and blue solutions, the violet is formed by a mixture of these, whilst the green is due to the condensation of the particles which give rise to the red and blue.

Hatschek and Simon have studied the reduction of gold in gels with a view of explaining the nature of gold in various ore deposits.[1]

When alcohol is added to the red solution obtained by the action of formaldehyde on auric chloride, the gold is precipitated in a form soluble in water (Zsigmondy).

239 *Purple of Cassius.*—This body, which is used in the preparation of ruby glass, was discovered by Andreas Cassius, who, however, did not publish anything on the subject, though his son of the same name published a pamphlet in 1685 entitled *De extremo illo et perfectissimo naturæ opificio ac principe terrenorum sidere, Auro, et admiranda ejus natura—cogitata, experimentis illustrata.* In the previous year, however, a Hessian mining official, Orschal, published a paper, *Sol Sine Vesta: or, Thirty Experiments to Draw out its Purple from Gold.* He declared that he had learned the process from Cassius, and that it consisted in precipitating gold with tin. After that time many investigations were made on this pigment without any satisfactory explanation of its chemical nature being arrived at. A variety of receipts was given for its preparation, in all of which gold chloride was precipitated by a mixture of stannous and stannic chlorides. This precipitate is, according to the mode of preparation, either of a dark purple-red or of a reddish-brown colour, but yields a brown powder on drying. The process by which the finest purple is obtained is, according to Fuchs, to add stannous chloride to a solution of ferric chloride until the yellow colour is changed to a pale green, and then to precipitate the gold solution with this mixture. The precipitate contains tin oxide in varying quantities, and some chemists have supposed that the compound is a gold stannate, but this view is contradicted by the fact that when purple of Cassius is dried and then triturated, the powder assumes a metallic lustre, and on heating does not evolve oxygen. On the other hand, it is found that the freshly precipitated and moist pigment is soluble in ammonia forming a purple-coloured liquid which deposits gold when it is exposed to light or is heated;[2] the excess of ammonia can also be removed by dialysis leaving

[1] *Trans. Inst. Min. and Met.*, 1912, **21**, 451.

[2] See also Müller, *J. pr. Chem.*, 1884, [2], **30**, 252.

a colloidal solution of gold and stannic oxide.[1] Mercury does not extract gold from purple of Cassius. A similar purple colour is obtained by adding excess of mercurous chloride or a mixture of mercurous chloride with barium sulphate in suspension to a solution of auric chloride,[2] whilst Moissan[3] has obtained it by the distillation in air of an alloy of gold and tin, when the tin burns to tin oxide and purple of Cassius is deposited in the cool parts of the tube. This chemist has also obtained similar purple substances by distilling gold with alumina, magnesia, zirconia, silica, lime, or other oxides, and concludes that purple of Cassius is a lake of tin oxide coloured by very finely divided gold. The literature respecting the purple of Cassius up to 1866 has been collected by J. C. Fischer.[4]

240 *Gilding.*—The art of gilding is mentioned by Moses, and Pliny states that objects of wood and marble are gilt by means of gold leaf, whilst metallic surfaces are gilt by help of quicksilver. Gold leaf is obtained from gold foil by hammering pieces, each having an area of a square inch and weighing six grains, first between sheets of vellum or tough paper, and afterwards between leaves of gold-beater's skin—a material prepared from the cæcum of the ox. The small cuttings and waste leaf are employed for the preparation of the shell gold used by painters.

A variety of methods is employed for gilding metals. In gilding by immersion the well-cleaned objects are dipped into a boiling solution of gold chloride and potassium bicarbonate; whilst in wash-gilding a gold amalgam is rubbed on the surface, the mercury afterwards driven off by heating and the surface either burnished, or deadened by being heated with a fused mixture of common salt, saltpetre, and lime, when a small quantity of chlorine is liberated which etches the gold. These older methods have now, however, been almost completely supplanted by the *electro-deposition of gold.* For this purpose a solution of gold cyanide in potassium cyanide is employed, a gold plate being used as the positive electrode. The colour of the deposited gold can be modified by adding to the gold solution salts of silver or copper, as well as both of these, when alloys are deposited.

241 *Alloys of Gold.*—Pure gold is very soft, and is soon worn

[1] Schneider, *Zeit. anorg. Chem.*, 1893, **5**, 80.

[2] Antony and Lucchesi, *Gazz.*, 1896, **26**, ii., 195.

[3] *Compt. rend.*, 1905, **141**, 977; see also Debray, *ibid.*, 1872, **75**, 1025, and Zsigmondy, *Annalen*, 1898, **301**, 361.

[4] *Dingl. Polyt. Journ.*, 1866, **182**, 39.

away by use. Hence, for the purpose of coinage, and for the use of the goldsmith, it is alloyed with copper or silver, or with both together, the resulting alloys being much harder than pure gold. Copper imparts to the gold a red colour, and lowers its fusing-point. This alloy was formerly called red-carat gold, because the fineness of a gold alloy used to be universally expressed in carats, 24-carat gold being pure gold. In England at the present time five legal standards exist for gold ware; 22-carat or standard gold, 18, 15, 12, and 9-carat gold, the meaning of this being that 24 parts by weight of the alloy contain 22, 18, 15, 12, and 9 parts of gold respectively.

In the case of the coinage, however, the fineness of gold is generally expressed in parts per 1,000. Thus, for instance, English standard gold, being 22-carat gold, has a fineness of 916·67. In the German, American, and Italian coinage standard gold is of 21·6 carats, or has a fineness of 900. Red-carat ornaments are frequently covered with a thin coating of pure gold by heating them and then dipping them for a short time in dilute nitric acid.

The alloys of gold and silver are called white alloys, and have a greenish-yellow colour if they do not contain too small a quantity of silver, whilst when the latter metal is present in larger amount the alloy assumes a yellowish-white shade. A gold-silver alloy of varying composition occurs naturally as electrum, often found in crystals belonging to the regular system and containing from 15 to 35 per cent. of silver.

Trinket gold contains both copper and silver. It is hard, and, according to the proportion of its materials, possesses either a yellowish-red or a whitish colour.

Various other alloys have been examined and described. Of these the aluminium-gold alloys are distinguished by the richness and variety of their colours.[1]

Gold also combines with arsenic, antimony, and bismuth, when heated with these elements. The addition of one part of the last named metal to 1,920 parts of gold is sufficient to render the gold brittle.

Gold-amalgam.—Gold readily combines with mercury, the mixture becoming solid when 15 per cent. of gold is present. Crystalline amalgams of varying composition can be obtained artificially, whilst others occur naturally in California, Columbia, and Victoria. The mercury may be almost entirely removed

[1] Roberts-Austen, *Proc. Roy. Soc.*, 1892, **50**, 367.

from these amalgams by distillation at a red-heat, but the gold retains 0·1 per cent. practically up to its melting point.

COMPOUNDS OF GOLD.

242 Gold forms two chief series of compounds, the auric compounds in which it is trivalent, and the aurous compounds in which it is monovalent. The best known salts are those of the halogen acids, and hydrocyanic acid. These readily form double salts, as do aurous sulphite and thiosulphate. Auric oxide has well-marked acidic properties, as have also the various sulphides of the metal. The compounds with the halogens, oxygen and sulphur are all decomposed into their elements by heat, whilst reducing agents very readily precipitate the metal from the solutions of its salts.

Gold and Oxygen.

243 Gold does not combine directly with oxygen, and the two compounds, aurous oxide, Au_2O, and auric oxide, Au_2O_3, are obtained from the corresponding halogen compounds. A third compound, auro-auric oxide, $(AuO)_n$, is formed by the partial decomposition of auric hydroxide at 160°. The substance formerly known as purple oxide of gold appears to be nothing but finely-divided gold, and the oxides Au_2O_4[1] and Au_2O_5 appear not to exist. All the oxides decompose into gold and oxygen when they are heated. Auric oxide acts towards strong bases as an acid-forming oxide, whilst it also forms salts with acids.

Gold Monoxide, Aurous Oxide, Au_2O.—The *hydroxide,* AuOH, is formed when the corresponding chloride is treated with cold dilute caustic potash (Berzelius), and when a solution of the trichloride is boiled with the potassium salt of acetic or another organic acid. It may be prepared pure by reducing potassium auribromide, $KAuBr_4$, with sulphurous acid, and then warming with dilute potash. It is a powder which when moist has a dark-violet colour, and becomes greyish-violet when dry. When freshly prepared it forms with cold water an indigo blue liquid[2] from which the oxide is removed when barium sulphate is precipitated in it.[3] It loses water at 200°, and is decomposed at 250° into gold and oxygen. When

[1] Prat, *Compt. rend.*, 1870, **70**, 842.
[2] Krüss, *Ber.*, 1886, **19**, 2541.
[3] Vanino, *Ber.*, 1905, **38**, 462.

treated with hydrochloric acid, it yields gold and the trichloride, slowly in the cold, more rapidly on boiling. Sulphuric acid and nitric acid do not act on it, but it is easily dissolved by aqua regia.

Gold Trioxide, Auric Oxide, Au_2O_3.—The substance termed calx of gold by the early chemists was nothing more than the finely divided metal. Bergman was the first to state that the precipitate produced by alkalis in the gold solution was dephlogisticated gold ; but the oxide was examined more carefully in 1806 by Proust, and in 1811 by Oberkampf. Gold trioxide is a brownish powder, obtained by carefully heating the hydroxide. If this be more strongly heated, it gives off oxygen, and is converted into a brown powder of metallic gold.

Gold Trihydroxide, Auric Hydroxide, $Au(OH)_3$, is best obtained by heating a solution of gold trichloride with an excess of magnesia, and well washing the precipitate with dilute nitric acid (Pelletier). The gold solution may also be treated with caustic potash until the precipitate which is formed is redissolved, and then the dark-brown solution boiled until its colour becomes light yellow, a slight excess of sulphuric acid added, and the precipitate washed. The hydroxide thus prepared always contains a little potash, and for this reason it is dissolved in concentrated nitric acid, again precipitated by water, and dried in a vacuum. According to Thomsen a better method is to precipitate the brown solution by Glauber's salt, when it is obtained in a form resembling precipitated ferric hydroxide. Gold trihydroxide when kept over phosphorus pentoxide is converted into a chestnut-brown powder of *auryl hydroxide*, AuO(OH), which at 140—150° yields auric oxide (Krüss).

When the hydroxide is warmed with alcoholic potash reduction occurs, and the metal is produced in the form of fine glistening scales, which are employed in miniature painting. It is a weak base, which dissolves slightly in concentrated sulphuric acid, and more readily in nitric acid, from which solutions it is again precipitated by the addition of water. It forms the corresponding halogen salts with hydrochloric and hydrobromic acids. Gold trioxide is also an acid forming oxide, and its salts are termed aurates.

Potassium Aurate, $KAuO_2,3H_2O$, is obtained in the form of small yellow needles by evaporating a solution of auric hydroxide in caustic potash in a vacuum ;[1] these are easily soluble in water

[1] See also Meyer, *Compt. rend.*, 1907, **145**, 805.

and have a strong alkaline reaction. It is very unstable, and its solution is used for gilding copper and other metals.

The other aurates are less completely investigated. The solution of the potassium salt yields precipitates with many metallic salts.[1]

Auroauric Oxide, $(AuO)_n$, is formed when auric hydroxide is heated at 160°. It is a dark yellowish-brown hygroscopic powder which loses oxygen at 173°.[2]

Gold and the Halogens.

244 Gold unites with chlorine and bromine directly to form the auric compounds, $AuCl_3$, $AuBr_3$, which are easily soluble in water. These readily combine with the halogen acids and their salts with monovalent metals or radicals to form complex substances such as aurichloric acid, $HAuCl_4$, and the aurichlorides. The salts of this acid with the organic bases, such as methylamine aurichloride, $NH_3(CH_3)AuCl_4$, are often used for the characterisation of the latter. Both the halogen compounds themselves and their compounds with the corresponding acids decompose when heated, metallic gold being finally left.

The aurous compounds are unstable and readily decompose when heated. They are insoluble in water, like the corresponding silver and cuprous compounds.

The substances described as auroauric chloride and bromide,[3] Au_2Cl_4 and Au_2Br_4, have been proved to be nothing but mixtures of metallic gold with the corresponding auric salt.

Aurous Chloride, AuCl, is best obtained by carefully heating the trichloride to about 175°. It is a yellowish powder of specific gravity 7·4,[4] which decomposes gradually into gold and chlorine at 185°, more rapidly at a higher temperature.

It is insoluble in water but is decomposed by it slowly in the cold, and more rapidly on heating, with formation of metallic gold and auric chloride. It dissolves in a solution of potassium bromide with formation of metallic gold and potassium aurichloride and auribromide.[5]

[1] Fremy, *Ann. Chim. Phys.*, 1851, (3), **31**, 480.

[2] Krüss, *Ber.*, 1886, **19**, 2541.

[3] Krüss and Schmidt, *Ber.*, 1887, **20**, 2634; *J. pr. Chem.*, 1888, (2), **38**, 77.

[4] Rose, *Journ. Chem. Soc.*, 1895, **67**, 881, 905; see also Campbell, *Trans. Far. Soc.*, 1907, **3**, 103.

[5] Lengfeld, *Amer. Chem. J.*, 1901, **26**, 324.

Liquid ammonia acts on aurous chloride at −28° to form the compound $AuCl,12NH_3$, which loses ammonia on warming, yielding $AuCl,3NH_3$, and this above 180° is decomposed with formation of ammonium chloride and gold.[1]

Potassium Aurochloride, $KAuCl_2$, is formed when potassium aurichloride, $KAuCl_4$, is heated. It forms a yellow mass, which is decomposed by water into gold, potassium chloride, and auric chloride.

Auric Chloride, or *Gold Trichloride,* $AuCl_3$.—The Latin Geber and all the later chemists were acquainted with the fact that gold dissolves in aqua regia. When this solution is evaporated to dryness a portion of the chloride is decomposed with formation of aurous chloride (Berzelius). In order to prepare the pure anhydrous chloride the best process is that proposed by Thomsen. It consists in acting upon gold powder with chlorine and treating the mass with a small quantity of water. When gently heated, any aurous chloride decomposes as before described, the metallic gold is filtered off, the solution evaporated gently, and then heated to 150°, when anhydrous auric chloride remains as a brown crystalline mass which is soluble in ether. The anhydrous chloride is also formed by heating gold leaf in chlorine to 300°, or by heating gold with liquid chlorine in a sealed tube at 100°.[2] Gold chloride is also formed when gold is treated with fuming hydrochloric acid in the presence of a trace of manganese chloride and the mixture is exposed to light.[3] It melts at 288° when heated in a sealed tube, and has the sp. gr. 4·3. When the brownish-red aqueous solution is evaporated until a crystalline film is formed on the surface, large dark orange-red crystals of $AuCl_3,2H_2O$ are deposited. These deliquesce in moist air, whilst they effloresce in dry air.

The chloride dissociates very slowly below 100°, more rapidly at higher temperatures, with formation of aurous chloride, chlorine, and gold. The dissociation pressure of the chlorine is about 1 atmosphere at 251°, and 4 atmospheres at 330°. In spite of this dissociation the chloride can be sublimed in a stream of chlorine at all temperatures up to 1,100°, the most rapid volatilisation taking place at the melting point.[4]

[1] Meyer, *Compt. rend.*, 1906, **143**, 280.

[2] Lengfeld, *Amer. Chem. J.*, 1901, **26**, 324.

[3] Berthelot, *Compt. rend.*, 1904, **138**, 1297.

[4] Debray, *Compt. rend.*, 1869, **69**, 985; Krüss, *Annalen*, 1887, **238**, 249; *Ber.*, 1887, **20**, 2634; Rose, *Journ. Chem. Soc.*, 1895, **67**, 881; Meyer, *Compt. rend.*, 1901, **133**, 815.

Very dilute aqueous solutions of auric chloride are decomposed on heating for some time, or on continued exposure to direct sunlight, metallic gold being precipitated and hydrogen peroxide formed in the solution.[1]

Gold chloride in solution is decomposed by charcoal, and Avery[2] has quantitatively determined the hydrogen chloride and carbon dioxide produced by the reaction, and considers that the equation proposed by König[3] is substantiated, thus:

$$4AuCl_3 + 6H_2O + 3C = 4Au + 12HCl + 3CO_2.$$

Gases occluded by charcoal, such as hydrogen and carbon monoxide, will, however, also reduce gold chloride.

According to Brusson,[4] charcoal adsorbs gold either when shaken with a solution of gold chloride, or when a solution is filtered through charcoal. In all cases, the gold was completely withdrawn from solution, chlorine being left behind.

Gold chloride is largely used in photography for toning silver prints, a process which consists in the replacement of the silver by metallic gold.

Aurichloric Acid or *Chloro-auric Acid*, $HAuCl_4$.—When hydrochloric acid is added to a neutral solution of auric chloride it becomes yellow, and the liquid then contains the above compound in solution. The same substance is obtained when gold is dissolved in aqua regia containing an excess of hydrochloric acid. When either of the above solutions is evaporated and allowed to stand over quick lime, long yellow needles of $HAuCl_4,3H_2O$ are deposited,[5] which deliquesce on exposure. The solution has a bitter taste, is poisonous, and colours the skin, nails, ivory, &c., a purple-red tint when exposed to light. This fact was mentioned in 1663 by Boyle as being one then not generally known.

Gold is precipitated quantitatively in solutions containing aurichloric acid by formaldehyde after neutralising with sodium hydrate.[6]

[1] Sonstadt, *Chem. News*, 1898, **77**, 74; *Proc. Chem. Soc.*, 1898, 179.
[2] *J. Soc. Chem. Ind.*, 1908, **27**, 255.
[3] *Chem. News*, 1882, **45**, 215.
[4] *Zeit. Chem. Ind. Kolloide*, 1909, **5**, 137.
[5] Weber, *Jahresber.*, 1867, 314; Schottländer, *Annalen*, 1883, **217**, 312; Schmidt, *Chem. Centr.*, 1906, ii., 855.
[6] Vanino and Hartl., *Zeit. Chem. Ind. Kolloide*, 1907, **1**, 272.

On adding silver nitrate to a solution of aurichloric acid, a brown precipitate is obtained thus:[1]

$$HAuCl_4 + 4AgNO_3 + 3H_2O = Au(OH)_3,AgCl + 4HNO_3.$$

By the action of ammonia, this is converted into fulminating gold, $Au(OH)_2.NH_2$.

Potassium Aurichloride, $KAuCl_4$.—When a strongly acid solution of auric chloride, to which the calculated quantity of potassium chloride has been added, is allowed to evaporate at a gentle heat, light-yellow monoclinic needles having the composition $2KAuCl_4,H_2O$ are deposited. On the other hand, when the neutral or slightly acid solution is employed, large transparent rhombic tablets of $KAuCl_4,2H_2O$ are formed, which easily effloresce on exposure. When heated these melt with evolution of chlorine, forming potassium aurochloride, $KAuCl_2$.

Sodium Aurichloride, $NaAuCl_4,2H_2O$, is obtained by dissolving common salt in a solution of auric chloride and concentrating the solution, when it is deposited in yellowish-red rhombic tablets or prisms, which do not alter on exposure.

Ammonium Aurichloride, NH_4AuCl_4, appears to have been prepared by the alchemists, who employed aqua regia containing sal-ammoniac for dissolving gold, and on cooling the solution obtained crystals which they considered to be a true gold vitriol. From the neutral solution large light-yellow rhombic tablets of the composition $2NH_4AuCl_4,5H_2O$ separate. These are tolerably permanent. From an acid solution, on the other hand, the salt $4NH_4AuCl_4,5H_2O$, crystallises in monoclinic plates. Both salts become anhydrous at 100°.

The chlorides of the calcium and magnesium groups, as well as those of manganese, nickel, cobalt, and thallium, also form crystalline aurichlorides.

Aurous Bromide, AuBr, is formed as a greenish-yellow micaceous powder when auribromic acid, $HAuBr_4$, is heated at 115°, but is decomposed at a higher temperature. It is insoluble in water, and hydrobromic acid decomposes it into gold and the compound from which it has been obtained. It dissolves in potassium cyanide solution without decomposition, and in ammonia with partial decomposition.[2]

Aurous bromide when acted on by dry ammonia gas at 18° yields the white compound $AuBr,2NH_3$, which is decomposed

[1] Jacobsen, *Compt. rend.*, 1908, **146**, 1213.
[2] Lengfeld, *Amer. Chem. J.*, 1901, **26**, 324

by heat into its elements, and by water with formation of ammonium bromide and gold.[1]

Auric Bromide, or *Gold Tribromide*, $AuBr_3$.—Finely-divided gold dissolves slowly in an aqueous solution of bromine (Balard). In order to obtain the anhydrous compound, bromine is allowed to act upon gold powder, and the tribromide is extracted from the product by ether. When the solution is evaporated at a low temperature, the tribromide remains behind as a black crystalline crust, which dissolves slowly in water. The concentrated solution is viscid and almost black (Thomsen).

When heated, auric bromide dissociates, forming a green mass of aurous bromide, and at higher temperatures this latter dissociates into its elements.[2]

Auribromic Acid, $HAuBr_4,5H_2O$, is formed when bromine is allowed to act upon gold powder, and as soon as the reaction is over, a quantity of hydrobromic acid, having a specific gravity of 1·38, equivalent to the quantity of gold present, is added, and then more bromine until the gold is completely dissolved. It crystallises in dark cinnabar-red flat needles, and melts at 77°.

Potassium Auribromide, $KAuBr_4,2H_2O$, is prepared by adding bromine to powdered gold in presence of the requisite amount of potassium bromide. It is also formed together with metallic gold when aurous bromide is dissolved in potassium bromide (Lengfeld). It forms reddish-purple monoclinic crystals. Similar compounds of the other soluble bromides are also known.[3]

Aurous Iodide, AuI, is formed when hydriodic acid acts upon gold oxide:

$$Au_2O_3 + 6HI = 2AuI + 3H_2O + 2I_2.$$

It is also formed when dry iodine is heated with metallic gold[4] between 50° and 114°, and also when the neutral trichloride is precipitated by a solution of three molecular proportions of potassium iodide, iodine being liberated. When finely-divided gold is boiled with hydriodic acid and a small quantity of nitric acid, and the filtrate allowed to run into hydriodic acid, a lemon-yellow coloured crystalline powder of aurous iodide is formed. It is when pure a very unstable white powder, which

[1] Meyer, *Compt. rend.*, 1906, **143**, 280.
[2] *Ibid.*, 1909, **148**, 346.
[3] Thorpe and Laurie, *Journ. Chem. Soc.*, 1887, **51**, 576.
[4] Meyer, *Compt. rend.*, 1904, **139**, 733.

assumes a green colour when exposed to the air and deposits a bright surface of metallic gold on the inside of the vessel in which it stands. The decomposition takes place more quickly on warming, and is complete at 190°. Aqueous acids decompose it only when heated.

Aurous iodide forms with either liquid or gaseous ammonia the compounds $AuI,6NH_3$ and AuI,NH_3, which are decomposed by heating or by addition of water.[1]

Auric Iodide, AuI_3.—When a neutral solution of auric chloride is added to one of excess of potassium iodide, the liquid becomes of a dark-green colour, and yields a green precipitate, which on agitation dissolves again, inasmuch as potassium auri-iodide is formed. If, however, more gold solution be added, a permanent precipitate is formed, and this, after washing, may be dried, but it evolves iodine, and is converted on standing into aurous iodide. It forms dark-coloured crystalline auri-iodides with the soluble iodides, but it is doubtful whether the free acid exists.[2]

Gold and Sulphur.

245 Gold does not combine directly with sulphur, but three sulphides corresponding in composition with the three oxides can be prepared indirectly. They are all dark-coloured powders which decompose into their elements when they are heated, and are soluble in the alkali sulphides.

Aurous Sulphide, Au_2S, is prepared by passing sulphuretted hydrogen into a solution of aurous cyanide in potassium cyanide and then acidifying. It forms a brownish-black powder which is soluble in water when it is freshly precipitated, but loses this property when it is dried. It is not attacked by hydrochloric or sulphuric acids, but dissolves readily in potassium cyanide. This sulphide is also formed, mixed with gold and sulphur, when sulphuretted hydrogen is passed into a hot solution of auric chloride.[3]

Sodium Aurosulphide, $NaAuS,4H_2O$, is obtained by heating metallic gold with sodium sulphide and sulphur, and treating the fused mass with water. The solution is filtered in an atmosphere of nitrogen and evaporated in a vacuum over sulphuric

[1] Meyer, *Compt. rend.*, 1906, **143**, 280.
[2] Johnston, *Phil. Mag.*, 1836, (3), **9**, 266.
[3] Hoffmann and Krüss, *Ber.*, 1887, **20**, 2369.

acid. Colourless, monoclinic prisms are then deposited which soon become brown on exposure to air. The same salt is formed when aurous or auro-auric sulphide is dissolved in sodium sulphide solution.[1]

That gold can be brought into solution by fusing it with liver of sulphur seems to have been known to Glauber, but Stahl, in his *Observationes Chymico-Physico-Medicæ*, is the first distinctly to mention this fact; and it may be added that he there explains that Moses burnt up the golden calf with alkali and sulphur, and gave the solution of liver of sulphur containing gold to the Israelites to drink.

Auro-auric Sulphide, AuS, is precipitated when sulphuretted hydrogen is passed into a cold neutral solution of auric chloride, the sulphuretted hydrogen being partially oxidised to sulphuric acid:[2]

$$8AuCl_3 + 9H_2S + 4H_2O = 8AuS + 24HCl + H_2SO_4.$$

It is a black powder which dissolves in sodium sulphide solution and is thereby reduced to aurous sulphide, the liquid being found to contain sodium aurosulphide and sodium disulphide.[3] It readily forms colloidal solutions in water and alcohol[4] and is dissolved by potassium cyanide. When left in contact with auric chloride it is reduced to metallic gold.[5]

Auric Sulphide, Au_2S_3, is a very unstable substance and cannot be prepared by passing sulphuretted hydrogen into a solution of auric chloride, nor by heating gold with sodium pentasulphide, as stated by Berzelius. It is formed when anhydrous lithium aurichloride is treated with dry sulphuretted hydrogen at –10°.[6] It is an amorphous, graphitic powder, has the specific gravity 8·754, and decomposes into gold and sulphur at 200°. It is decomposed by the sulphides of ammonium but dissolves in sodium sulphide forming sodium aurisulphide. Like the other sulphides it is soluble in potassium cyanide. Yellow crystals of the composition AuS_3,NH_4 have been prepared by allowing a mixture of aqueous auric chloride and ammonium polysulphide to stand for several days at 18°.[7]

[1] Ditte, *Compt. rend.*, 1895, **120**, 320.

[2] Levol, *Ann. Chim. Phys.*, 1850, (3), **30**, 355; Hoffmann and Krüss, *Ber.*, 1887, **20**, 2074.

[3] Ditte, *Compt. rend.*, 1895, **120**, 320.

[4] Schneider, *Ber.*, 1891, **24**, 2241; 1892, **25**, 1164.

[5] Antony and Lucchesi, *Gazz.*, 1889, **19**, 545.

[6] Antony and Lucchesi, *Gazz.*, 1890, **20**, 601; 1891, **21**, ii., 209.

[7] Hofmann and Höchtlen, *Ber.*, 1904, **37**, 245.

Sodium Aurous Sulphite, $3Na_2SO_3,Au_2SO_3,3H_2O$, is formed when sodium hydrogen sulphite is added to a boiling alkaline solution of sodium aurate, or when this solution is saturated with sulphur dioxide at 50°. It is very easily oxidisable, but in presence of free sulphur dioxide the solution may be heated to boiling without decomposition occurring. When this solution is precipitated by alcohol the salt is obtained as a purple powder which appears yellow or green by reflected light. The corresponding ammonium salt, together with a compound of the formula $(NH_4)_2SO_3,3(NH_3Au)_2SO_3,3H_2O$, has also been described.[1]

Potassium Auric Sulphite, $5K_2SO_3,Au_2(SO_3)_3,5H_2O$, is formed when potassium sulphite solution is poured into a solution of potassium aurate, the above salt separating from the brown liquid in beautiful yellow needles. It is very unstable, and easily decomposes with separation of gold.

Sodium Auro-thiosulphate, $3Na_2S_2O_3,Au_2S_2O_3,4H_2O$, is formed by the gradual addition of a neutral 2 per cent. solution of auric chloride to a solution containing four molecular proportions of sodium thiosulphate. It is necessary to wait after each addition until the red liquid which is formed becomes colourless. The salt is formed according to the equation:

$$8Na_2S_2O_3+2AuCl_3=(3Na_2S_2O_3+Au_2S_2O_3)+2Na_2S_4O_6+6NaCl.$$

It is then precipitated with strong alcohol, and any sodium chloride and tetrathionate which may be present removed by repeated solution in water and precipitation with alcohol. It is also formed by the action of sodium thiosulphate on gold in the presence of oxygen. It crystallises in colourless needles, which have a sweet taste. Its solution is not reduced by ferrous sulphate or oxalic acid, nor is it at once decomposed by hydrochloric acid, or by dilute sulphuric acid, although this occurs on standing.

When barium chloride, and afterwards alcohol, are added to its solution a precipitate of the corresponding barium salt is obtained, from which a solution of the acid auro-thiosulphate, $3H_2S_2O_3,Au_2S_2O_3$, is obtained by addition of the requisite quantity of sulphuric acid. This salt is not known in the anhydrous state, but the solution can be evaporated in the air to a syrupy consistency.

[1] See also Rosenheim, Hertzmann, and Pritze, *Zeit. anorg. Chem.*, 1908, **59**, 198.

The above compounds do not exhibit the reactions either of the aurous salts or of the thiosulphates, and hence it is assumed that they contain a compound radical, whose hydrogen salt is the last-named compound. They may, therefore, be written $H_3S_4O_6Au$ and $Na_3S_4O_6Au,2H_2O$. The extraction of gold from auriferous silver ores by means of sodium thiosulphate depends on the formation of these compounds.

Gold Telluride, $AuTe_2$, has been found to occur associated with silver telluride in the minerals sylvanite, calaverite, and krennerite, in Kalgoorlie, Western Australia, and in Colorado and Dakota.[1]

Gold and Nitrogen and Phosphorus.

246 *Auro-diamine* or *Fulminating Gold,* $Au(NH)NH_2$.—The preparation of this compound was described with great accuracy in the *Last Testament* of Basil Valentine. He obtained it by dissolving gold in *aqua regia* mixed with *sal-ammoniac,* precipitating with *sal-tartari* (potashes), and subsequently washing with water. He then says: "Dry the gold calx in the air where no sun shines, and especially not over the fire, for as soon as this powder is exposed to a little warmth it ignites and does a great deal of damage, for it then explodes with such great power and might that no man can withstand." He then describes its properties, and, amongst others, that it loses its explosive power when heated with sulphur. The name of fulminating gold (aurum fulminans) was given to it by Beguin in 1608. It was, however, also known under other names, and was used as a medicine. Angelus Sala, writing in the first half of the seventeenth century, mentions that no fulminating gold can be prepared if aqua regia made with hydrochloric acid be employed instead of that made with sal-ammoniac, and Glauber says that the preparation obtained by means of volatile alkali (carbonate of ammonia) fulminates much more strongly than that made with *oleum tartari* (carbonate of potash). In spite of these observations, few chemists believed that the volatile alkali took part in the composition of the substance, and a great number of erroneous observations were made on the subject of the composition of fulminating gold.[2] Even Black in 1756

[1] Frenzel, *Tsch. Min. Mitth.*, 1897, **17**, 288; Chester, *Amer. J. Sci.*, 1898, [4], **5**, 375; Smith, *Trans. Amer. Inst. Mining Eng.*, 1897, **26**, 485; Pittman, *Records Geol. Survey N.S.W.*, 1898, **5**, 203, and others.

[2] Kopp, *Geschichte der Chemie,* **4**, 210.

stated that the explosion was due to the sudden evolution of fixed air, although Kunkel, a very accurate observer, had already pointed out the true cause. For in his *Laboratorium Chymicum*, which appeared in 1716, fourteen years after his death, he described the preparation of fulminating gold, and discussed the various reactions which took place. He then continued: "Once I precipitated the gold with *oleum tartari*, distilled the menstruum to dryness, and then edulcorated; and I thus obtained a fine gold calx which became brown but did not fulminate at all; when, however, the same substance was imbibed several times with *spiritus urinæ* and very gently dried, it exploded violently." He also said that when this substance was imbibed and afterward distilled with oil of vitriol, an acid sal-volatile sublimed in the neck of the retort. "Hence," he added, "thou canst see whence the power in the *aurum fulminans* comes, namely from the *sal-volatile concentratum*." This view was confirmed by the experiments of Bergman and Scheele, who considered fulminating gold to be a compound of ammonia and gold calx. Hence the Lavoisierians termed this compound *oxide d'or ammoniacal*. The composition of this body was subsequently more exactly investigated by Dumas,[1] and later by Raschig.[2]

When ammonia is added to a solution of auric chloride, a mixture of fulminating gold with *auric imidochloride*, Au(NH)Cl, is precipitated and cannot be obtained quite free from chlorine even by prolonged digestion with ammonia. Pure fulminating gold is therefore best prepared by the action of concentrated ammonia on auric hydroxide. When dried over phosphorus pentoxide it has the composition $2AuN_2H_3,3H_2O$, and is a dirty olive-green powder which explodes with great violence, either on percussion or when heated. When it is boiled with water a portion of the nitrogen is evolved in the form of ammonia, and the powder becomes so unstable that it can scarcely be touched without undergoing decomposition. It is decomposed by hydrochloric acid with formation of auric chloride and ammonium chloride:

$$AuN_2H_3 + 5HCl = AuCl_3 + 2NH_4Cl.$$

With sulphuric acid, on the other hand, it appears to unite, forming an extremely explosive *sulphate*, $(AuN_2H_3)_4H_2SO_4$. Both aurous and auroauric oxides are acted on by ammonia

[1] *Ann. Chim. Phys.*, 1855, **44**, 167.
[2] *Annalen*, 1886, **235**, 341.

with formation of compounds analogous to fulminating gold. The aurous compound, *sesquiauramine*, has the formula NAu_3,NH_3, is not very explosive, and loses half its nitrogen when boiled with water, yielding *triauramine*, NAu_3. The derivative of auroauric oxide has the formula $N_2Au_3,5H_2O$, and is violently explosive.

Phosphides of Gold.—Gold and phosphorus do not combine at a dull red heat, but the compound Au_3P_4 is formed by heating gold at 400° in phosphorus vapour, the tube being rapidly cooled while still full of vapour. It is a grey mass which decomposes on heating above the temperature at which it is formed, and is attacked by chlorine and aqua regia.[1] A phosphide of the formula AuP is formed by the action of phosphine on an ethereal solution of auric chloride.[2]

Gold and Carbon.

247 *Aurous Acetylide* or *Aurous Carbide*, Au_2C_2.—This compound is obtained as a yellow powder when acetylene is passed into a solution of aurous thiosulphate. It is very explosive when dry, and is decomposed by hydrochloric acid with formation of aurous chloride and acetylene, whilst it is decomposed into its elements by boiling with water.[3]

Aurous Cyanide, AuCN.—This compound is obtained by the addition of hydrochloric acid to a solution of the potassium double salt, and evaporation on the water-bath, the residue being washed in the dark. It is a fine yellow powder, showing iridescent colours, and consists of microscopic hexagonal tablets insoluble in water, and, in the dry state, unalterable in the air. It is not attacked by the single acids, but dissolves readily in aqua regia, as well as in ammonia, ammonium sulphide, and sodium thiosulphate.

Potassium Aurocyanide, $KAu(CN)_2$.—This compound, largely used in electro-gilding, is best obtained as follows: 7 parts of gold are dissolved in aqua regia, precipitated by ammonia, the fulminating gold well washed and brought into a boiling solution of 6 parts of pure potassium cyanide. The solution is then filtered and allowed to cool, when, if it is not too dilute,

[1] Granger, *Compt. rend.*, 1897, **124**, 498.

[2] Cavazzi, *Gazz.*, 1885, **15**, 40.

[3] Berthelot, *Ann. Chim. Phys.*, 1866, [4], **9**, 425; Mathews and Watters, *J. Amer. Chem. Soc.*, 1900, **22**, 108.

the salt separates out in colourless rhombic pyramids having a pearly lustre. These have a saline and at the same time metallic taste, and are soluble in 7 parts of cold, and in rather less than half their weight of boiling water. The mother-liquor of these salts contains as impurity potassium chloride and potassium carbonate, and yields on evaporation impure crystals. These are, therefore, decomposed with hydrochloric acid as above described, and the resulting aurocyanide dissolved in potassium cyanide.

Potassium aurocyanide is also formed when finely divided gold is treated in the presence of air with a solution of potassium cyanide [1] (p. 499):

$$4Au + 8KCN + O_2 + 2H_2O = 4AuK(CN)_2 + 4KOH.$$

Ammonium Aurocyanide, $NH_4Au(CN)_2$, is obtained by mixing a solution of the foregoing salt with one of ammonium sulphate, and removing the potassium sulphate by precipitation with alcohol. The crystals have a disagreeable metallic taste, and are easily soluble in water, alcohol, and ether.

Auric Cyanide, $Au(CN)_3$, is not certainly known in the free state, but exists in combination with hydrocyanic acid and other cyanides.[2]

Auricyanic Acid, $2HAu(CN)_4,3H_2O$, is obtained from the potassium salt by precipitation with silver nitrate. The precipitated silver salt is washed with cold water and decomposed by somewhat less than the requisite quantity of hydrochloric acid. The filtrate yields on evaporation tabular crystals which are easily soluble in water, alcohol, and ether.

Potassium Auricyanide, $2KAu(CN)_4,3H_2O$, is obtained by mixing hot concentrated solutions of gold trichloride and potassium cyanide. On cooling it crystallises in large colourless efflorescent tablets. It is used for electro-gilding.

Ammonium Auricyanide, $NH_4Au(CN)_4,2H_2O$, is formed when auric hydroxide is dissolved in ammonium cyanide. It forms either four- or six-sided tablets which are easily soluble in water and alcohol, but not in ether.

Aurous Thiocyanate is only known in combination with other thiocyanates. *Potassium aurothiocyanate*, AuSCN,KSCN, is obtained with evolution of thiocyanic acid, when a neutral gold

[1] Elsner, *J. pr. Chem.*, 1846, **37**, 333; Johnston, *Phil. Mag.*, 1836, [3], **9**, 266.

[2] Himly, *Annalen*, 1842, **42**, 340; and Gmelin, *Handbook*, **8**, 41.

solution is poured into a hot solution of potassium thiocyanate. It crystallises in yellow obtuse prisms. When hydrochloric acid is added to the solution copper-red needles separate out, and silver nitrate precipitates the *double silver gold thiocyanate*, AuSCN,AgSCN. Ammonia also produces a white precipitate of *aurammonium thiocyanate*, $(AuNH_3)SCN$.

Auric Thiocyanate is not known in the free state, but if a solution of gold trichloride be precipitated with potassium thiocyanate in the cold, an orange-yellow precipitate of $KAu(SCN)_4$ is thrown down, which crystallises in slender needles and is partially decomposed by hot water.

Detection and Estimation of Gold.

248 When a gold compound is heated on charcoal in the reducing flame, a yellow malleable bead is obtained which dissolves in aqua regia. If this solution be dropped on to filter paper and one drop of stannous chloride added, a purple red colour is observed. Gold can be readily detected in its solutions inasmuch as it is obtained in the metallic state by reducing agents, the well-washed precipitate being dissolved and the solution tested with stannous chloride. This is best done by pouring the boiling solution which is supposed to contain gold into a small quantity of concentrated stannous chloride solution. If gold be present, the precipitated stannous hydrate has a purplish colour. One part of gold in 100,000,000 of water can thus be detected.[1]

In the ordinary method of analysis gold is precipitated along with tin, antimony, arsenic, and platinum. The method adopted for its separation is described under the last of these.

The spark spectrum of gold has been mapped by Kirchhoff, Thalén, Huggins, and Krüss. The brightest lines are 6,277 5,960, 5,955, and 5,836 in the orange and yellow, and 5,230 and 4,792 in the green and blue; there are also several lines in the violet and ultra-violet. Gold compounds do not impart any tint to the non-luminous gas flame.

Assay of Gold Ores and Bullion.—The amount of gold contained in an ore is usually ascertained by fusing the ore with red-lead or litharge, charcoal, sodium carbonate, and borax. In this way a button of lead is obtained which contains all the gold and silver of the ore. This button is then cupelled, the residual

[1] Rose, *Chem. News*, 1892, **66**, 271.

bead of gold-silver alloy weighed, recupelled with more silver if necessary, treated with nitric acid, and the gold which remains weighed. In order to determine the value of gold bullion it is cupelled with lead with addition of so much silver that the quantity of the latter is about two and a half times that of the gold present. A gold-silver alloy is thus obtained which is rolled out and then boiled with nitric acid of specific gravity 1·26. The residual gold cornet having been well washed is placed in a small crucible and heated in a muffle to a point just below that at which gold melts, in order to render it coherent, after which it is cooled and weighed.

The assaying of gold is an operation of much importance and one in which great accuracy is needed. The errors attaching to the process are chiefly (1) errors in weighing, (2) loss of gold by absorption in the cupel and by volatilisation, (3) slight solution of the gold by the acid, (4) and most important, the presence of a portion of silver in the gold cornet, together with occluded gases. In order to compensate for these various errors, an allowance, called the *surcharge*, is made on each assay, the value of this allowance being determined by special experiments with known amounts of pure gold. In this way, and by carrying out all the processes with unvarying uniformity, as well as by making the assay on a number of samples placed in different parts of the muffle, very great accuracy can be attained. When every precaution is taken the limit of accuracy which can be obtained with high standard alloys appears to be one part in 50,000.[1]

Gold has also been estimated electrolytically by depositing it from solutions of its salts in the presence of potassium cyanide or thiocyanate.

The Atomic Weight of Gold was first determined with accuracy by Berzelius,[2] who ascertained the quantity of mercury necessary to precipitate gold from its chloride, and obtained as the mean of two experiments the number 196·4. At a later period[3] he determined the relation between gold and potassium chloride in potassium aurichloride, $KAuCl_4$, and obtained the number 196·69, whilst Levol[4] found the number 196·49 by reducing a solution of pure auric chloride with sulphur dioxide and determining the relation between the precipitated gold and the sulphuric acid which was formed.

[1] Rose, *Journ. Chem. Soc.*, 1893, **63**, 700. [2] *Schweiggers, Journ.*, **7**, 44.
[3] *Berz. Jahresber.*, **25**, 41. [4] *Ann. Chim. Phys.*, 1850 [3], **30**, 355.

The atomic weight has also been determined by Thorpe and Laurie, Krüss, and Mallet. The first-named chemists [1] started with potassium auribromide which was carefully heated to convert it into metallic gold and potassium bromide. The relation of gold to potassium bromide in this mixture was then determined, as well as the amount of silver necessary to precipitate the potassium bromide corresponding to a known amount of gold, and the amount of silver bromide thus formed. The mean result of these experiments was 197·28. Krüss [2] arrived at a somewhat lower number, 197·13, by the analysis of weighed amounts of the same salt. Mallet [3] finally obtained the number 197·22, intermediate between those of Thorpe and Laurie, and Krüss, by the analysis of auric chloride, auric bromide, and potassium auribromide. Other determinations by somewhat less reliable methods yielded him rather high numbers. The atomic weight is now (1913) taken as 197·2.

[1] *Journ. Chem. Soc.*, 1887, **51**, 866.
[2] *Ber.*, 1887, **20**, 207; *Annalen*, 1887, **238**, 30, 242.
[3] *Proc. Roy. Soc.*, 1890, **46**, 71.

GROUP II.

Sub-group (*a*).—The Alkaline Earth Metals:
Calcium.
Strontium.
Barium.
Radium.

Sub-group (*b*).—The Magnesium Group:
Glucinum (Beryllium).
Magnesium.
Zinc.
Cadmium.
Mercury.

249 The metals of this group are divalent in almost all their compounds. An apparent exception is the element mercury, which in addition to the normal derivatives forms a series of salts in which each atom of the metal replaces only one atom of hydrogen. It appears probable, however, that two atoms of the element are present in the molecules of these compounds, united to form a divalent group Hg_2''.

Some of the other metals form halogen compounds corresponding in composition with the mercurous compounds, but these are as yet but little known. All the metals form a basic oxide, which has the general formula $M^{II}O$, and also yield the corresponding hydroxide $M^{II}(OH)_2$, which in the case of the metals of sub-group (*a*) is soluble, and in that of the metals of sub-group (*b*) almost insoluble, in water. All of these elements combine directly with oxygen fairly readily, forming the divalent oxide.

In the table given on pp. 50–1, it will be seen that

glucinum occurs in the same sub-group as calcium, strontium, and barium; in its general properties, however, it is more closely allied with magnesium and zinc, and it is therefore described together with these metals.

The element radium probably belongs to this group, but it is described later on among the radioactive elements.

THE ALKALINE EARTH METALS.

250 The name earth was used by the older chemists to designate all those non-metallic substances which were insoluble in water and did not undergo alteration when exposed to a high temperature. It was afterwards observed that some of these, such as lime and magnesia, were closely allied to the alkalis, inasmuch as they possessed an alkaline reaction and neutralised acids. These bodies were therefore termed *terræ alcalinæ*, and this name was subsequently also applied to baryta and strontia. As the other compounds of magnesium resemble the corresponding ones of zinc, cadmium, and glucinum more nearly than those of barium, strontium, and calcium, this metal is now no longer regarded as belonging to this group, the term "metals of the alkaline earths" being therefore confined to the metals contained in the oxides lime, strontia, and baryta.

The alkaline earths, like the alkalis, were supposed to be elementary bodies until Davy, in the year 1807, showed that each earth was a compound of a metal and oxygen.

The metals themselves very readily oxidise in moist air and decompose water at the ordinary temperature with evolution of hydrogen and formation of the hydroxide. The oxides fuse only at the temperature of the electric furnace, and combine with moisture with great avidity forming the hydroxides, the solubility of which in water increases with the atomic weight of the metal. They also form peroxides having the formula $M^{II}O_2$, that of barium being obtained by the direct union of barium monoxide and oxygen. Like the alkali metals they unite with hydrogen to form hydrides, and they all combine directly with nitrogen to form nitrides. The salts for the most part crystallise well; the carbonates, phosphates, and sulphates are either very sparingly soluble or insoluble in water, as are also their salts with many organic acids.

CALCIUM. Ca = 40.07.

251 The very early application of mortar to building purposes shows that the ancients were well acquainted with the properties of lime and its preparation by the burning of limestone. In the writings of Dioscorides and Pliny we find a description given of the process of lime-burning, as well as of that of slaking lime.

Calcium occurs very widely diffused in nature, especially as the carbonate, which occurs in various forms, such as calc-spar, aragonite, chalk, marble, limestone, coral, &c. United with magnesium carbonate, as magnesium limestone or dolomite, it forms whole mountain ranges, and this compound, when crystallised, is known as bitter-spar. Many other minerals contain calcium carbonate in isomorphous mixture; amongst these may be mentioned chalybite or brown-spar, $(Ca,Mg,Fe,Mn)CO_3$; mangano-calcite, $(Mn,Ca,Mg)CO_3$; plumbocalcite, $(Ca,Pb)CO_3$, &c. Calcium also occurs in large quantity as sulphate, either as the anhydrous compound, termed anhydrite, $CaSO_4$, or in the hydrated form, as selenite or gypsum, $CaSO_4,2H_2O$. Calcium phosphate, combined with calcium chloride or calcium fluoride, occurs in the well-known minerals apatite and osteolite. Calcium borate is also found in nature combined with many other metallic borates, whilst silicate of calcium occurs as an almost invariable constituent of all silicates. The solid constituents found in river and spring waters also consist mainly of calcium carbonate or calcium sulphate, and these, as well as phosphate and fluoride of calcium, are found in sea-water. The behaviour of these calcium salts during the evaporation of sea-water, and the forms in which they occur in mineral deposits which have been produced in this way, have been very fully dealt with by van't Hoff.[1]

Calcium salts form a never-failing component of the bodies of plants and animals, and cannot be replaced by any other salts. They accumulate in the leaves of plants; the roots and seeds, as a rule, yield only small quantities of them. The bones and teeth of animals contain large amounts of calcium phosphate, together with some carbonate and fluoride. Egg shells and the shells of mollusca, on the other hand, chiefly contain calcium

[1] *Zeit. anorg. Chem.*, 1905, **47**, 244.

carbonate. Calcium occurs also in the sun, in meteorites, and in certain of the fixed stars.

Preparation of Metallic Calcium.—Calcium was first prepared by Davy by the electrolysis of calcium chloride in the presence of mercury, the calcium remaining as a metallic powder upon heating the amalgam thus obtained. It was first obtained in a coherent metallic mass in 1856 by Matthiessen,[1] who electrolysed a mixture of the chlorides of calcium and strontium with a small amount of ammonium chloride in a porcelain crucible, the anode consisting of carbon, and the cathode of a thin iron wire, so that a high current density could be obtained. The metal prepared in this way had a yellowish colour and was not pure but probably contained calcium nitride and some strontium. The electrolysis of the chloride also yielded an impure product (Frei),[2] as did the action of sodium on the iodide[3], and of a mixture of zinc and sodium on the chloride.[4]

Calcium was first prepared in the pure state by Moissan[5] in 1898 by the electrolysis of the fused iodide and by heating calcium iodide with a large excess of sodium. The calcium separates from the sodium on cooling in white crystals, and the excess of sodium is then removed by the action of alcohol, which acts upon the sodium before the calcium.

Both of these processes were costly, and the economical production of metallic calcium remained an unsolved problem until in 1902 it was found that the metal could be obtained comparatively easily by the electrolysis of calcium chloride provided that the temperature of the fused salt was kept as low as possible. This was effected by Ruff and Plato[6] by using a mixture of 83·5 parts of calcium chloride with 16·5 of calcium fluoride, which melts at 655°. Borchers and Stockem[7] carried out the electrolysis in a special form of cell and obtained the metal in the form of a spongy mass, which was then pressed together under the surface of the molten electrolyte, removed and melted under calcium chloride. The metal is now prepared as a coherent metallic mass on a moderately large scale from the chloride with or without admixture of fluoride. An iron rod is employed as the cathode, and this is gradually raised as

[1] *Journ. Chem. Soc.*, 1856, **8**, 28. [2] *Annalen*, 1876, **183**, 367.
[3] Liés Bodart and Jobin, *Ann. Chim. Phys.*, 1858, [3], **54**, 364.
[4] Caron, *Annalen*, 1860, **115**, 355.
[5] *Compt. rend.*, 1898, **126**, 1753. [6] *Ber.*, 1902, **35**, 3612.
[7] *Zeit. Elektrochem.*, 1902, **8**, 757 ; see also Arndt, *ibid.*, 1902, **8**, 861.

the electrolysis proceeds, drawing with it the adhering calcium, the metal being protected from the action of the air by the layer of fused salt with which it is covered.[1] It is thus obtained in the form of irregular cylinders sometimes weighing more than a quarter of a kilogram, and is at present (1913) sold in this form at about fifteen shillings per kilogram. Poulenc Frères employ an electrode of fused aluminium and obtain an alloy containing 97 per cent. of calcium. Metallic calcium has not yet found any important technical application.

Properties of Calcium.—Calcium as prepared by the foregoing method contains about 0·4—1 per cent. of impurities. It is of a pure silver-white colour, melts at about 800°, and has the density 1·52—1·59. It sublimes even below its melting point when heated in a vacuum, and condenses as a crystalline layer on the cooler parts of the vessel. It is malleable and somewhat harder than lead. A fresh surface soon becomes yellowish in the air, but retains its lustre in dry air. The metal decomposes water slowly, and acts vigorously on acids. Calcium reacts with alcohols, particularly on heating, producing alkyloxides, $Ca(OAlk)_2$.[2] It burns brilliantly when heated in oxygen, is attacked by chlorine and sulphur at 400°, and combines readily, when heated, with nitrogen, phosphorus, silicon, and other non-metals.[3]

When the metal prepared by electrolysis is hammered, mild explosions accompanied by showers of sparks occur, the cause of which has not yet been ascertained.[4] Alloys of calcium with other metals decompose water when they contain more than 11% of calcuim.[5]

COMPOUNDS OF CALCIUM.

Calcium and Oxygen.

252 *Calcium Monoxide* or *Lime*, CaO, is formed in the pure state by the ignition of the pure carbonate, as Iceland- or calc-

[1] Goodwin, *Proc. Amer. Phil. Soc.*, 1905, **43**, 381 : Wöhler, *Zeit. Elektrochem*, 1905, **11**, 612; Rathenau, *Zeit. Elektrochem.*, 1904, **10**, 508; Tucker and Whitney, *J. Amer. Chem. Soc.*, 1906, **28**, 84.

[2] Perkin and Pratt, *Journ. Chem. Soc.*, 1909, **95**, 159.

[3] Moissan, *Compt. rend.*, 1898, **127**, 584 ; 1899, **128**, 384 ; Arndt, *Ber.*, 1904, **37**, 4733; Moissan and Chavanne, *Compt. rend.*, 1905, **140**, 122.

[4] Doermer, *Ber.*, 1906, **39**, 211.

[5] Baar, *Zeit. Elektrochem.*, 1911, **70**, 352.

spar, or white marble, in a crucible in a current of indifferent gas; otherwise the decomposition is not complete (p. 129).

On the large scale lime is burnt in kilns, the interiors of which are usually egg-shaped. The limestone is mixed up with coal or other combustible matter, one bushel of coal generally sufficing to make five or six bushels of lime. In some cases an arch is formed over the fire-grate with lumps of limestone, the kiln filled up with smaller pieces, a fire kindled below the arch, and this kept up for thirty-six to forty-eight hours. The kiln is then allowed to cool, the lime removed, and a fresh charge introduced. An improved and continuous process of lime-burning is now often employed in which the charge of limestone and coal is added from time to time at the upper part of the kiln, and the quicklime withdrawn at the lower part. A great saving of fuel is thus effected, and the smoke which is always given off from the common kiln is, in the improved kiln, drawn into a high chimney and completely burnt.

Pure lime is a white amorphous mass, having a specific gravity of 3·30; it shows signs of fusion in the oxy-hydrogen flame and can readily be melted and boiled in the electric furnace, a current of about 300 amperes at 50—70 volts being sufficient to maintain 500 g. of lime in ebullition; the melting point is about 1900°. The vapour condenses in the electric furnace in cubes and acicular prisms composed of aggregates of cubes, which have the sp. gr. 3·40 and gradually pass into a second crystalline modification which is doubly refracting.[1] It is also obtained crystallised in cubes by heating calcium nitrate in a porcelain flask.[2] On exposure to the air it combines with moisture, passing into the hydroxide, $Ca(OH)_2$, which then absorbs carbon dioxide. When water is poured on to quick lime the latter is converted into the hydroxide with great evolution of heat, the temperature rising in some cases as high as 150°. The evolution of heat may be well shown by strewing a few grains of gunpowder on to the lime whilst it is being slaked, when the powder will take fire. Lime which has been fused slakes only after remaining in contact with water for two or three days.[3] Although lime unites so readily with water it is in absence of this a very inert substance; thus it does not combine to an appreciable extent

[1] Moissan, *Compt. rend.*, 1892, **115**, 1034; 1902, **134**, 136. Compare Jouve, *Compt. rend.*, 1901, **132**, 1117.

[2] Brügelmann, *Ann. Phys. Chem.*, 1877, **2**, 466.

[3] Oddo, *Atti. R. Accad. Lincei*, 1896, [5], **5**, i., 361; Gautier, *Compt. rend.*, 1899, **128**, 939.

with dry chlorine, carbon dioxide, sulphur dioxide or oxides of nitrogen below 300—350°, whereas it is readily acted on by these substances in presence of moisture.[1] Dry hydrogen chloride begins to attack it at 40°.[2]

The most important use of lime is in the preparation of mortars and cements for building purposes, and its value for these purposes depends upon the nature of the limestone from which it has been prepared. The lime obtained from pure limestone slakes readily and is termed a "fat" lime, but if the limestone contains magnesia it only forms a thin mixture with water, and is termed a "poor" lime. When the quantity of magnesia rises to 25—30 per cent. the product is almost useless for building purposes. If the limestone used contains silica in considerable quantity, the resulting lime yields a mortar which hardens under water; it is known as hydraulic lime, and the mortar obtained from it as hydraulic mortar (p. 565). The presence of clay in the limestone frequently causes it to vitrify if too strongly heated, a hard crust of silicates being formed on the surface which causes it to slake very slowly. Such lime is said to be "dead burnt."

Ordinary mortar is a mixture of one part of lime made into a paste with water and mixed with three to four parts of sharp sand, the completeness of the subsequent hardening being dependent on the proper admixture of the ingredients. Mortar sets sufficiently to give stability to a structure in a few days, this being brought about almost entirely by the loss of water. It thus becomes porous, and the lime is then gradually attacked by the carbon dioxide of the air, which converts it slowly but completely into calcium carbonate, the mortar gradually hardening, and cementing the sand and building material together. Many years or even centuries elapse before the maximum of hardness is reached, and it appears that at the same time an extremely slow combination of the silica and lime takes place; thus Petzholdt[3] found 2·1 per cent. of combined silica in a mortar 100 years old, and 6·2 per cent. in a sample 300 years old, the lime originally used only containing at most 0·11 per cent. Under ordinary circumstances, however, this action plays no part in the hardening process.

In addition to its use for building purposes lime is used for

[1] Veley, *Journ. Chem. Soc.*, 1893, **63**, 821; 1894, **65**, 1.
[2] Veley, *Ber.*, 1896, **29**, 577.
[3] *J. pr. Chem.*, 1839, **16**, 91; **17**, 464.

the purposes of drying gases and liquids, and in numerous analytical processes, and also, when slaked, for the purification of coal-gas (Vol. I., p. 873), and the manufacture of caustic soda and bleaching powder.

Calcium Hydroxide, $Ca(OH)_2$.—This substance, also known as *slaked lime*, is obtained, as already stated, by the action of water on quick lime. It is a white impalpable powder, having a specific gravity of 2·078 (Filhol). Calcium hydroxide is likewise obtained as a white precipitate, when a solution of caustic potash or soda is added to a tolerably strong solution of calcium chloride. If a very strong or saturated solution of calcium chloride be employed in the above experiment, the whole mass becomes solid. This fact was observed in 1686 by Francisco Lana, and described by him as the "chemical miracle." Calcium hydroxide dissolves more readily in cold than in hot water; 100 parts of water at 10° dissolve 0·29 part, at 100°, 0·06 part (Maben),[1] at 150°, 0·017 part, and at 190°, 0·008 part (Herold).[2] The clear solution, evaporated in a vacuum over sulphuric acid, deposits the hydroxide either in the form of small tablets or of small prismatic crystals.

The solution of calcium hydroxide, usually known as lime water, possesses an alkaline reaction and taste. It quickly absorbs carbon dioxide from the air, and is used in medicine and in the laboratory. As the ordinary slaked lime often contains small quantities of baryta and strontia together with soluble salts of the alkalis, it is usual to treat the powder several times with water and only to employ the last solution.

Milk of Lime is calcium hydroxide suspended in water.

Calcium Dioxide, CaO_2, was discovered by Thénard, who obtained it by precipitating lime water with hydrogen dioxide. In order to procure the substance in the pure state the hydrogen dioxide must be added in excess to lime water. The precipitate at 13—14° possesses the composition $CaO_2,8H_2O$, and consists of microscopic tetragonal tablets or prisms, which are sparingly soluble in water and insoluble in alcohol;[3] at a slightly higher temperature $CaO_2,2H_2O$ is produced.[4] On exposure to the air the crystals effloresce, and when heated to 130° they lose their water, leaving behind a light powder of the anhydrous oxide.

[1] *Pharm. J.*, [3], 1883-4, **14**, 505. See also Guthrie, *J. Soc. Chem. Ind.*, 1901, **20**, 223.

[2] *Zeit. Elektrochem.*, 1905, **11**, 417.

[3] *Ann. Chim. Phys.*, 1818, **8**, 313.

[4] de Forcrand, *Compt. rend.*, 1900, **130**, 1250, 1308, 1388.

When further heated the substance loses half its oxygen without fusing.

Technically it is manufactured by mixing and then compressing $Ca(OH)_2$ with Na_2O_2.[1] The pressed product is then treated with ice water. The dehydrated powder is used as an oxidising agent and antiseptic. It contains 13·5 per cent. of available oxygen, and a considerable amount of calcium hydroxide.[2]

Calcium and Hydrogen.

253 *Calcium Hydride*, CaH_2, is produced when metallic calcium is heated in a nickel boat to dull redness in a current of hydrogen. It forms a fused mass of slender transparent plates, has the sp. gr. 1·7, and does not decompose appreciably at 600° in vacuo. It is readily decomposed by water, yielding the hydroxide and hydrogen:

$$CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2.$$

It burns brillantly when heated in the air or oxygen, acts as a vigorous reducing agent, and is attacked by the halogens, sulphur, and phosphorus, when heated.[3] It is made technically by heating calcium in hydrogen in horizontal retorts, and is known as hydrolith. One kilogram, when treated with water, yields about one cubic metre of hydrogen.[4]

Calcium and the Halogens.

254 *Calcium Fluoride*, CaF_2, occurs as the mineral fluor-spar, which has from early times been used in the fluxing of ores, whence its name is derived. Agricola says "Fluores lapides gemmarum similes sed minus duri, qui ignis calore liquescunt"; and then further: "Dum metalla excoquuntur, adhibere solent, reddunt enim materiam in igne non paulo fluidiorem."

Fluor-spar occurs largely in Derbyshire in veins, especially in the celebrated limestone caves in the Castleton valley. It is there found as a coloured variety which is commonly known as *Blue John*, and one of these large caverns is termed the Blue John cave. It is also found in Saxony

[1] German Patents, 128617, 132706. *Cf.* also French Patent, 364249.
[2] Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, **25**, 298.
[3] Moissan, *Compt. rend.*, 1898, **127**, 29.
[4] Jaubert, *Compt. rend.*, 1906, **142**, 788.

and in many other countries. It crystallises in cubes and octahedra, and in combinations of these two forms, or in other forms belonging to the regular system. In the pure condition it is colourless; in general, however, it has a blue, violet, red, green, yellow, or brown colour, the cause of which, as in the case of coloured rock salt (p. 253), is not fully understood. Those samples which have a bright colour are worked up into vases, dishes, cups, &c. Calcium fluoride also occurs in small quantity in the ashes of certain plants, in bones, in the enamel of the teeth, in sea-water, and in the water of certain mineral springs. It is very nearly insoluble in water and dilute acids, melts at 1330°, and has the sp. gr. 3·18.

When precipitated calcium fluoride, obtained by mixing a solution of calcium chloride with one of a soluble metallic fluoride, is heated with water slightly acidified with hydrochloric acid, the precipitate is found to consist of microscopic octahedra.[1]

The property which fluor-spar possesses of becoming luminous when heated, giving rise to the term fluorescence, was first mentioned by Elsholz in 1677, and further described by Leibnitz in 1710.

Calcium Chloride, $CaCl_2$.—Isaac Hollandus in the fourteenth century describes, under the name of *sal-ammoniacum fixum*, a substance which he obtained by heating together sal-ammoniac and lime. Homberg in 1693 noticed that this salt, when fused, became phosphorescent, and hence it was long known as Homberg's phosphorus. Calcium chloride is found in solution in sea-water, and in many mineral springs. It also occurs as a constituent of a few minerals, such as tachhydrite, $CaCl_2,MgCl_2,12H_2O$, and apatite, $3Ca_3(PO_4)_2,(CaCl_2,CaF_2)$.

In order to prepare pure chloride of calcium, Iceland-spar, chalk, or white marble is dissolved in hydrochloric acid until the latter is nearly saturated. Chlorine water is then added, in order to oxidise any iron or manganese compounds which may be present. These impurities are next precipitated by the addition of milk of lime, and the precipitate is filtered off. The slightly alkaline solution is then acidified with hydrochloric acid, and the solution evaporated either to the point of crystallisation or to dryness. Chloride of calcium is obtained on the large scale as a by-product in several manufacturing processes, as in that of potassium chlorate, in the ammonia-soda process the Weldon chlorine process, &c.

[1] See also Defacqz, *Compt. rend.*, 1903, **137**, 1251.

The hydrated salt crystallises from a saturated solution in large hexagonal prisms, which have the composition $CaCl_2,6H_2O$. These melt at 30·2°, and deliquesce rapidly in the air, forming a thick liquid, to which the name of *oleum calcis* was formerly given. The crystals dissolve in water, producing a considerable diminution of temperature, the eutectic temperature being −55°. Heated to 200° this hydrate loses four molecules of water, and a white porous hygroscopic mass remains behind. If this hydrate is heated more strongly, the anhydrous salt is obtained which is largely used as a means of drying gases and organic liquids. This last melts at about 780°, and solidifies on cooling to a crystalline mass, which has a specific gravity of 2·26 and is also used as a desiccating agent.

When a solution of 103—127 parts of calcium chloride in 100 parts of water is cooled to 18—38°, a hydrate of the formula $CaCl_2,4H_2O$ separates out; it exists in two modifications, the more stable compound being less soluble in water than the other. The stable modification passes into the dihydrate, $CaCl_2,2H_2O$, at 45·3°, and the labile modification into the same hydrate at 38·4°; at 175·5° the monohydrate separates from the solution, and at 260° this is replaced by the anhydrous salt.[1]

100 parts of water dissolve

at	0°	10°	20°	40°	60°	80°	100°	170°	200°	260°
	59·5	65·0	74·5	115·3	136·8	147	159	255	311	347

parts of $CaCl_2$ (Roozeboom). Calcium chloride is also very readily soluble in alcohol.

A solution of 50 parts of the anhydrous salt in 100 parts of water boils at 112°, one containing 200 parts boils at 158°, and one containing 325 parts boils at 180°. Such solutions are employed as baths for constant temperatures above 100°.

Calcium chloride absorbs dry ammonia, giving rise to a voluminous powder having the composition $CaCl_2,8NH_3$, which, on exposure to the air, on solution in water, or on heating, loses ammonia, and which takes fire when thrown into chlorine gas.

If calcium chloride solution be boiled with slaked lime and the solution filtered hot, a basic salt, which is known as *calcium oxychloride*, separates out on cooling in long white needle-shaped crystals, having the composition $ClCa{\cdot}O{\cdot}Ca(OH),7H_2O$. The halogen salts of calcium form compounds of the

[1] Roozeboom, *Zeit. physikal. Chem.*, 1889, **4**, 31.

formulæ $CaCl_2,2ICl_3$, and CaI_4, analogous to the polyhalogen derivatives of rubidium and cæsium [1] (pp. 370, 374).

Calcium Bromide, $CaBr_2$, melting at 765°, and *Calcium Iodide*, CaI_2, melting at 740°, are salts very similar in their properties to calcium chloride.

Calcium Subchloride.—When the spongy calcium obtained by the methods of Borchers and Stockem is melted in presence of calcium chloride, the molten metal is found to be surrounded by a mass of transparent, red pleochroitic crystals.[2] These appear to consist of a subchloride of calcium; they have the composition CaCl, and react with water with formation of calcium chloride, calcium hydroxide, and hydrogen. An analogous *subiodide* was observed by Moissan.

The pure subchloride is prepared by heating calcium chloride with an equivalent of metallic calcium in a steel cylinder to 900—1000° for four hours.[3] The *subiodide* and *subfluoride* have also been prepared.

Chloride of Lime or *Bleaching Powder.*—This well-known bleaching agent and disinfectant is obtained as a dry powder by the action of chlorine on slaked lime.

The action of chlorine on milk of lime is analogous to its action on potash, a solution of calcium hypochlorite and chloride being obtained:

$$2Ca(OH)_2+2Cl_2=CaCl_2+Ca(OCl)_2+2H_2O,$$

and it was supposed by Balard in 1834 that the solid powder was also a mixture of chloride and hypochlorite, his views being for some time generally accepted. It was, however, pointed out by Fresenius [4] that a substance containing so much calcium chloride must be far more hygroscopic than bleaching powder is found to be, and a number of other constitutional formulæ were proposed, the most important being those of Stahlschmidt [5] and Odling.[6]

According to Stahlschmidt's supposition the action of chlorine on slaked lime takes place in the following manner:

$$3Ca(OH)_2+2Cl_2=2ClO\cdot Ca\cdot OH+CaCl_2+2H_2O.$$

[1] Weinland and Schlegelmilch, *Zeit. anorg. Chem.*, 1902, **30**, 134; Meyer, *ibid.*, 1902, **30**, 113.

[2] *Zeit. Elektrochem.*, 1902, **8**, 757.

[3] Wöhler and Rodewald, *Zeit. anorg. Chem.*, 1909, **61**, 54.

[4] *Annalen*, 1861, **118**, 317.

[5] *Dingl. Polyt. Journ.*, 1876, **220**, 243. [6] *Manual of Chemistry*, **1**, 56.

On addition of water the calcium chloride dissolves and the basic hypochlorite decomposes into hypochlorite and free lime.

According to Odling's formula the calcium is combined with the negative radicals of both hydrochloric and hypochlorous acid, as shown by the formula $Cl.Ca.OCl,H_2O$, and this compound by the action of water is resolved into calcium chloride and hypochlorite:

$$2Cl.Ca.OCl = CaCl_2 + Ca(OCl)_2.$$

The subject has been carefully investigated by Lunge in conjunction with Schaeppi and Naef,[1] and the results of their investigations have shown that the latter view is probably the more correct one. By careful preparation it is possible to obtain a powder containing 44 per cent. of available chlorine (*i.e.*, chlorine which is evolved when an acid is added), whilst according to Stahlschmidt's formula the maximum quantity of available chlorine is only 39 per cent. Further, no calcium chloride can be extracted from bleaching powder by means of alcohol, and a large part of the chlorine may be expelled by the action of carbon dioxide, which could scarcely be the case if it contained calcium chloride. O'Shea[2] has also shown that for every molecule of CaO two atoms of chlorine can be added, and that of this chlorine half is available for the formation of hypochlorous acid, which further confirms Odling's formula. Dreyfuss[3] has raised objections to this formula, but his conclusions have been shown by Lunge and Schoch to be untenable.[4]

All bleaching powder, however, yields a certain amount of calcium hydroxide when it is treated with water, and the formation of this is not accounted for by Odling's formula. By some investigators this lime is regarded as existing free in the bleaching powder, having been protected from the action of the chlorine by a layer of the chlorinated compound. According to Ditz,[5] this is not the case, the lime forming an essential part of the bleaching compound. He considers that bleaching powder is formed by a series of reactions, the first of which is represented by the following equation:

$$(1)\ 2Ca(OH)_2 + Cl_2 = CaO,Cl.Ca.OCl,H_2O + H_2O.$$

[1] *Dingl. Polyt. Journ.*, 1880, **237**, 63; *Annalen*, 1883, **219**, 129; 1884, **223**, 106.

[2] *Journ. Chem. Soc.*, 1883, **43**, 410.

[3] *Bull. Soc. chim.*, 1885, [2], **41**, 600.

[4] *Ber.*, 1887, **20**, 1474.

[5] *Chem. Zeit.*, 1898, **22**, i., 7; *Zeit. angew. Chem.*, 1901, **14**, 3, 25, 49, 105; 1902, **15**, 749.

This can be experimentally realised at $-10°$ to $-15°$, and the resulting powder loses one molecule of water below 100°, whilst the compound $CaO,Cl.Ca.OCl,H_2O$, which is left behind at this temperature, decomposes at 130—180°, losing one atom of oxygen and only losing the second molecule of water at a red heat. It is also completely decomposed by moist carbon dioxide, all the chlorine being liberated. At a somewhat higher temperature the action of chlorine on slaked lime containing not more than $\frac{1}{2}$ per cent. of uncombined water produces a greater degree of chlorination, and this represents the second stage in the formation of bleaching powder:

(2)a. $2[CaO,Cl.Ca.OCl,H_2O]+2H_2O=$
$2Ca(OH)_2+2[Cl.Ca.OCl,H_2O]$.

b. $2Ca(OH)_2+Cl_2=CaO,Cl.Ca.OCl,H_2O+H_2O$.

The final product at the close of this stage, therefore, has the composition $CaO,Cl.Ca.OCl,H_2O+2[Cl.Ca.OCl,H_2O]+H_2O$.

This process may theoretically be indefinitely repeated, but in practice it is limited by the amount of uncombined water present in the slaked lime, and does not proceed beyond the stage at which the product has the composition $CaO,Cl.Ca.OCl,H_2O+6[Cl.Ca.OCl,H_2O]+H_2O$. These higher products undergo a complicated decomposition when they are heated, oxygen and chlorine being evolved, and chlorate and chloride formed. They are also decomposed even by dry carbon dioxide, but the whole of the chlorine is not evolved.

The complex $Cl.Ca.OCl,H_2O$ has probably a greater molecular weight than corresponds with the simple formula, but its constitution has not yet been settled.

Tiesenholt,[1] on the other hand, maintains the older view of Balard, and regards the reaction between lime and chlorine as reversible. Other views are held by some investigators, and the whole question cannot yet be regarded as definitely determined.[2]

The Manufacture of Bleaching Powder.

255 *History of the Manufacture of Hypochlorites.*—Chlorine gas was first employed for bleaching in 1785 on the suggestion of Ber-

[1] *J. pr. Chem.*, 1901, [2], **63**, 30; **65**, 512.

[2] Winteler, *Zeit. anory. Chem.*, 1902, **33**, 161; *Zeit. angew. Chem.*, 1903, **16**, 32; Tarugi, *Gazz.*, 1904, 34, ii., 254; Schwartz, *Zeit. angew. Chem.*, 1906, **20**, 138.

thollet, and the first hypochlorite was manufactured for bleaching purposes in 1789, at Javel, near Paris, where chlorine was absorbed in potash liquor, whence the name "eau de Javel" which is still used for potassium hypochlorite (see p. 333). These processes were introduced into England in 1796; in 1798 "bleach liquor" was being made by absorbing chlorine in milk of lime, and in 1799 Tennant, of Glasgow, originated the absorption in *dry* hydrate of lime, thus making for the first time "bleaching powder," which sold at £140 per ton, but the price soon fell to £60. The chlorine was made directly from a mixture of salt, sulphuric acid, and manganese dioxide. In 1825—*i.e.*, immediately after the introduction of the Leblanc soda-process into the district—hydrochloric acid became available as a raw material, and the price was reduced to £27. Many methods were proposed to use or recover the manganese contained in the waste still liquors, but they proved unsuccessful, until Weldon by his process of 1866, and subsequent improvements, achieved such success, that in 1870 the price of bleaching powder fell to £8 10*s.* The present price (1913) of 35% bleaching powder is £5 7*s.* 6*d.* The combined Leblanc-Weldon process grew rapidly, attaining in 1877 an annual output of nearly 100,000 tons in the United Kingdom alone. Another method of generating chlorine utilised in making bleaching powder was the Deacon process, introduced and perfected from 1868 to 1876; the special method of utilising the weak chlorine thus obtained is described in the following pages; only a small portion of the total bleaching powder is, however, now made by Deacon's process. The latest source of chlorine for the manufacture of bleaching powder is the electrolysis of chloride solutions. Hargreaves and Bird's process, started in 1892 at Farnworth, and now carried on in works erected in 1900, at Middlewich, and Castner's process, originating in Oldbury in 1891, and installed in 1897 on a large scale in Runcorn, both electrolyse sodium chloride (see p. 313). In a third process, proposed by Mond about 1898, zinc chloride solution is electrolysed (see p. 310). Abroad other processes besides the above are being utilised, and potassium chloride is electrolysed in a number of works. In 1900 there were in Europe twenty-five electrolytic alkali works producing chlorine, with a total of 40,000 horse-power, and in the United States, three works with 5,200 horse-power; since then the output has been considerably increased.

Electrolytic methods have also recently been introduced for manufacturing hypochlorite solutions, and though such processes as yield only one product, namely, the hypochlorite solution, cannot compete with any of the previously mentioned processes which make simultaneously two products, yet they are serviceable to paper-pulp and bleach works which are far removed from bleaching powder works. The first suggestion for such a process was due to Watt, a paper-maker, in 1851, but it was impracticable, as dynamo-electric machines were not then obtainable. Lidoff and Tichomiroff in 1882 introduced a process, and exhibited yarn and cloth bleached by it. Hermite in 1883 claimed for his process,[1] electrolysis of calcium chloride or magnesium chloride solutions, special advantages over bleaching with bleaching powder, and from this time forward a vast number of processes have been patented, by Kellner, Haas and Oettel, Schoop, and Atkins, all of whom use sodium chloride solutions, and many papers have been published on the theory of the process (see p. 254).[2]

In 1910, about 6,660 horse-power was employed in the manufacture of liquid bleach, which produced about 13,120 kilos. of active chlorine per day.

Manufacture of Bleaching Powder.—The details of the methods for preparing the chlorine required in the manufacture of bleaching powder are described under the head of chlorine (Vol. I., p. 178). For this purpose the chlorine should be as free as possible from carbonic acid, originating either from calcium carbonate in the native manganese, or in Weldon mud, or from the furnaces in the Deacon process, or from the corrosion of the carbon anodes, where such are used in electrolytic methods. Further, the chlorine must be particularly free from hydrochloric acid and any large quantity of water vapour, and this is effected by passing the gas through a long range of earthenware pipes cooled by exposure to the air. The lime employed requires to be specially free from clay, magnesia, iron, and manganese compounds, the last two of which discolour and gradually decompose the bleach, both when dry and when dissolved.

The absorption of the chlorine is effected in three different

[1] *J. Soc. Chem. Ind.*, 1885, **4**, 673; 1887, **6**, 170.

[2] Full details of these processes are given in *Monographien über angewandte Elektrochemie*, Band 8; Engelhardt, *Hypochlorite und elektrische Bleiche*, 1903, Band 17; Abel, *Hypochlorite und elektrische Bleiche* (Theoretischer Teil), 1905, Band 38; Ebert and Nussbaum (*Praktish-angewandter Teil*), 1910.

kinds of apparatus, (1) large roomy chambers, (2) small chambers filled with trays, (3) revolving cylinders, and of these the first is the most usual.

Ordinary Chambers.—Two only out of a set of four or more are shown in Fig. 122, one being in end elevation and the other in section, while Fig. 124 shows the same in plan, but with the middle portions cut out, as the total length is 80 to 100 feet. These chambers are made of timber framing, supporting sheet lead, so that the supports are all outside the lead; the floor is covered with asphalt or with earthenware tiles.

The chlorine is brought from the still (Figs. 121, 123) to the chambers by the central main, and can be directed into any chamber by removing the two hydraulic caps closing the main and the chamber, and substituting a bent pipe dipping into the two water lutes. The displaced air escapes from the lute F until the smell of chlorine is observed, when the bend is used to connect the chamber, as shown in Fig. 124, to the second pipe main adjacent, by which the gas is carried to any other chamber desired, entering at the lute corresponding to F and leaving by the open lute G until the chlorine begins to escape here also, when by placing a bend in G the gas may be directed by the main adjacent to any third chamber in the series, where the last trace of chlorine is absorbed. The main G also serves as an exhaust pipe for drawing off the last remaining quantities of the unabsorbed chlorine when the operation is complete. The exterior view, Fig. 122, shows the doors and bolts and the gallows for the swinging of the doors, which are closed gas-tight by a paste of tar and china clay, or of lime and water.

The chambers described rest upon the ground. Much labour and inconvenience is avoided by building the chamber on pillars and having a number of hopper holes in the floor, closed while the bleaching powder is being made, with lids which are covered with lime, to prevent leakage of chlorine. When the powder is ready to pack, the lids are lifted, the powder shovelled down the hoppers and through a sacking or rubber sleeve which connects the hopper to the head of the cask. In these chambers the absorption of chlorine occupies about six days. After the lime has been placed upon the floor of the chamber to the thickness of about four inches, it is deeply furrowed like a ploughed field by a special rake, and the chlorine is turned on until the chamber is full, as seen by means of windows placed at each end, the air and any surplus chlorine

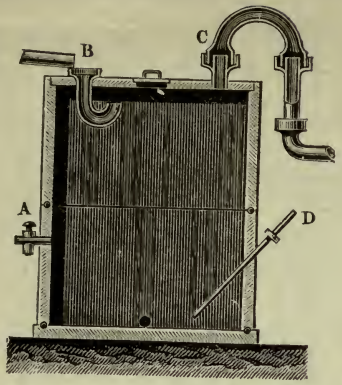


FIG. 121.

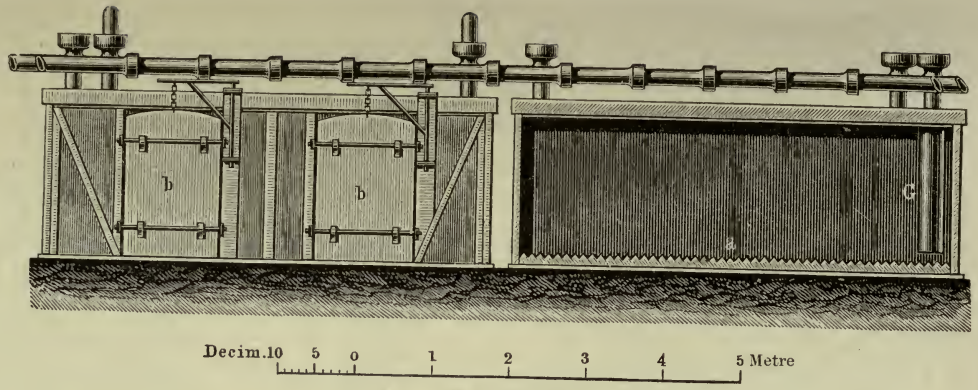


FIG. 122.

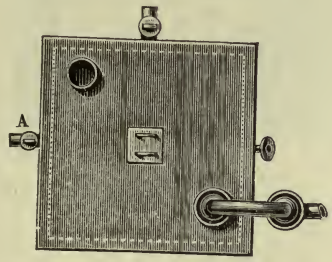


FIG. 123.

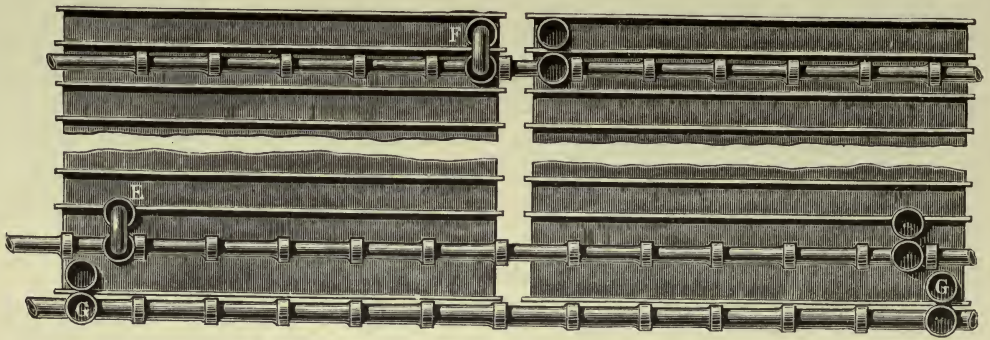


FIG. 124.

escaping from the chamber and passing by the circulating pipes into the next or some other chamber where there is more fresh lime. When the first chamber has been filled with chlorine it is allowed to stand for about two days, during which time the gas is completely or nearly completely absorbed, and the lime is then found to contain on an average from 25 to 30 per cent. of available chlorine. Any unabsorbed gas is then drawn off by means of the exit pipe (G), the doors are opened, and workmen enter and turn the material, as the bottom layers are still very weak in chlorine; the doors are then closed and more chlorine is admitted, the quantity being sufficient to raise the amount of chlorine, after absorption for a second period of two days, to from 35 to 37 per cent. The unabsorbed chlorine is drawn off as before, and the powder packed and sent to market.

Much trouble has been experienced in removing the residual chlorine from the finished chambers, and fatal results have followed the premature opening of the doors, so that in 1886 a penalty was imposed for opening the doors before the chlorine contents of the chamber had been reduced to less than two and a half grains per cubic foot. In the same year Brock and Minton introduced their lime sprinkler, a portable machine in which a stream of lime dust is allowed to fall on to a rapidly revolving paddle with a vertical shaft, so that the dust is scattered in a cloud and the gases are also put in motion and help to carry the lime dust to a considerable distance. Every 30 feet in the length of the chamber a large luted cap is provided, and these are lifted in turn, the sprinkler inserted, and one or more hundredweight of lime sprinkled in, when the absorption of the chlorine is almost instantaneous and so complete that the residual chlorine need not exceed one grain per cubic foot.

A different form of bleaching powder chamber was devised by Deacon for use with the specially weak chlorine made by his process. The principles of this process have already been referred to (Vol. I., p. 178). These chambers are shown in elevation and section in Figs. 125 and 126. The gas, containing only 5 to 7 per cent. chlorine, passes in through the tube (A), being drawn over the lime by means of exhausters. Each block, of which less than one half is shown in Fig. 125, is divided by vertical walls into fourteen sections; each section contains sixteen slate shelves 20 feet long by 4 feet wide, with a gap in the middle covered by a small loose piece, and the lime

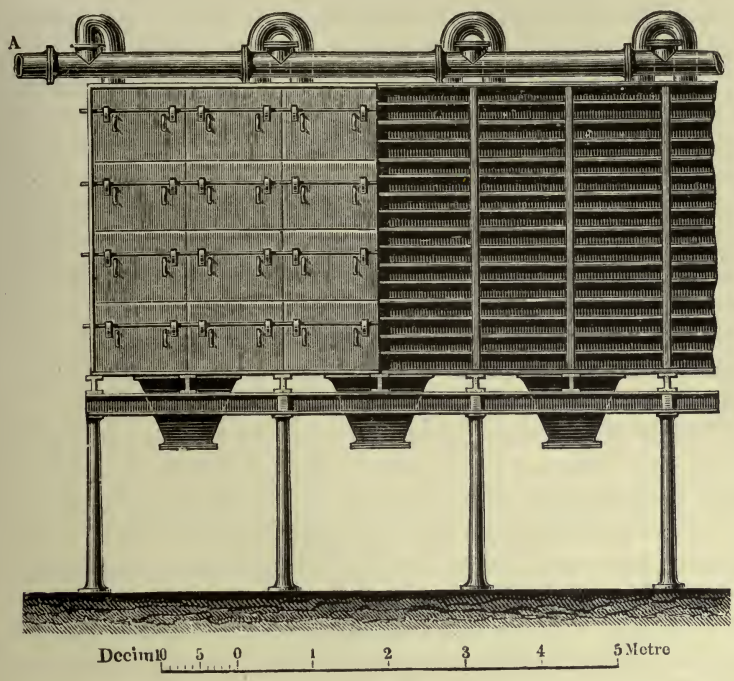


FIG. 125.

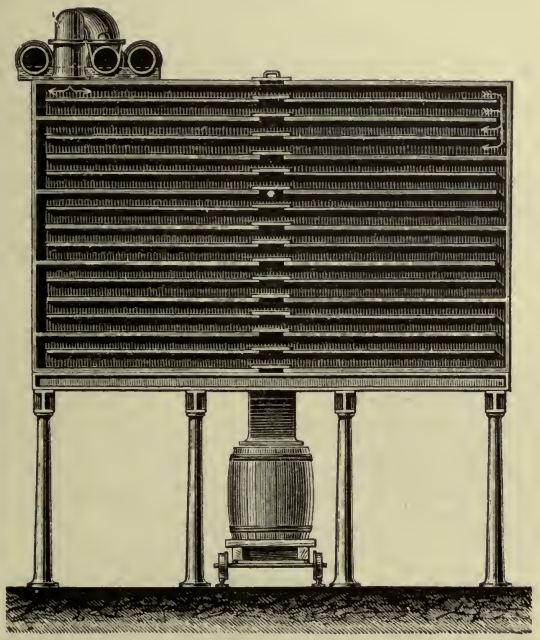


FIG. 126.

is spread on these shelves to the depth of about five-eighths of an inch. Part of the elevation shows the doors, which form the sides of the chamber, in position; the other part shows the arrangement of the shelves seen when the doors are down. The end section (Fig. 126) shows the mode in which the shelves are arranged and the way in which the chlorine is divided into streams during its passage downwards over the lime. The gas then passes upwards over a similar set of shelves, and thence by the gas mains into the next chamber. When the lime in one chamber has come up to strength, the small plates on each shelf are removed, and the bleaching powder is pushed into a barrel placed on a tramcar beneath, and in this way the product is easily packed.

During recent years several forms of continuous mechanical apparatus have been successfully adopted, in which the slaked lime is transported in a continuous stream by single or double conveyors in an opposite direction to the stream of chlorine, the finished bleaching powder being delivered direct into casks, thus avoiding the disagreeable task of hand packing.[1]

A complete analysis by Pattinson of good commercial chloride of lime giving 36·00 per cent. available chlorine shows the constituents to be:—

Odling's calcium chloro-hypochlorite, $Ca\begin{cases} Cl \\ OCl \end{cases} + H_2O$.	73·65
Ditto, but decomposed into the chlorate mixture $5CaCl_2 + Ca(ClO_3)_2$	0·67
Calcium hydroxide, $Ca(OH)_2$ . . . . . 20·17 . .	22·55
Impurities from all the slaked lime employed, 2·38 . .	
Moisture originally present as such in the slaked lime or in the chlorine employed	3·13
	100·00

By the Griesheim-Elektron process a product containing 80–90 per cent. of active chlorine is produced. Milk of lime is saturated with chlorine, filtered and the solution rapidly evaporated in vacuum. The calcium hypochlorite crystallises out and on drying in vacuum a stable salt is obtained.[2]

Properties of Bleaching Powder.—Commercial bleaching powder contains on an average 35—37 per cent. of available

[1] Mond, *Nature*, 1896, **54**, 477. [2] German Patent, 188524, 1906.

chlorine, and forms a white powder, which absorbs moisture and carbon dioxide on exposure to the air. When kept, it undergoes a very slow and steady decomposition, for reasons which are at present undetermined; in closed bottles this decomposition is sometimes such as to burst the bottle by the gases evolved. When added to water it is apt to clot together into lumps, but by agitation it forms a creamy liquid which deposits a large amount of insoluble slaked lime, &c., whilst the clear solution contains calcium chloride, hypochlorite, chlorate, and some hydroxide.

When a slight excess of acid is added to a solution of bleaching powder, the whole of the chlorine is evolved in the free state, the hydrochloric acid and hypochlorous acid first formed acting on one another in the manner already described (Vol. I., p. 350):

$$CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2CaSO_4 + 2HCl + 2HClO,$$
$$2HCl + 2HClO = 2Cl_2 + 2H_2O.$$

Bleaching Processes.—Bleaching powder is largely employed in the bleaching of cotton, linen, and paper pulp. The methods employed are often exceedingly complex, varying not only with the nature of the material to be bleached, but also with the use to which the bleached goods are afterwards to be put, but in all cases the main impurities in the fibre are removed not by hypochlorite, but by treatment with an alkali. Thus by hot alkali solutions—*i.e.*, sodium carbonate or calcium hydroxide, but best of all caustic soda—various waxy, fatty, resinous, gummy, mucilaginous and colouring matters are extracted, and the fibre is thereby greatly lightened in colour, the loss in weight being about 8 per cent. in the case of cotton, 25 per cent. in that of flax, and 50 per cent. in that of esparto grass. The fibre is then treated with hypochlorite solution, which is rapidly converted into the chloride by acting upon certain of the residual organic impurities: this action is so energetic that if not properly controlled it may oxidise the cellulose itself, rendering the fibre brittle and useless. Strong solutions of bleaching powder are therefore never employed, and often very weak ones are used, containing as little as 0·1 per cent. of available chlorine. Such a solution may be allowed to act for a few hours, when the final whitening is frequently obtained by transferring the goods to a very dilute acid bath to remove basic colouring matters, and as chlorine is liberated from the residual hypochlorite in the fibre, the process is known

by the workmen as a "stinking sour." To obtain brilliant whites it is often necessary to repeat the operations several times, and this is particularly necessary in the case of linen.

The amount of available chlorine in bleaching powder is usually ascertained by adding to a solution of a known quantity a standard solution of sodium arsenite until the liquid no longer turns iodised starch paper blue, the arsenite being thus oxidised to arsenate. Precautions must, of course, be taken to obtain a fair average sample for analysis; for this purpose many samples must be taken from various places and packages, taking care to obtain due proportions of fine powder and of lump, and these must be mixed without undue exposure to the air.

Calcium Chlorate, $Ca(ClO_3)_2$, is formed by leading chlorine into hot milk of lime, but cannot be obtained pure in this manner. The pure salt is obtained by neutralising calcium carbonate with chloric acid, and crystallises with $2H_2O$ in rhombic prisms which deliquesce in moist air; 100 parts of water at 18° dissolve 177·8 parts of $Ca(ClO_3)_2$.

Calcium and Sulphur.

256 *Calcium Monosulphide*, CaS, is obtained by heating the sulphate with powdered coal, or by leading sulphuretted hydrogen or a mixture of carbon dioxide and the vapour of carbon disulphide over incandescent lime (Schöne). It forms a yellowish-white mass insoluble in water, which in moist air smells of sulphuretted hydrogen. When prepared in the electric furnace it is formed in cubes which have the sp. gr. 2·4—2·5.[1]

Calcium monosulphide is luminous in the dark after it has been exposed to light. This fact was noticed in the year 1750 by Marggraf, who obtained the sulphide by calcining gypsum with combustible matter. In 1768 Canton described a method of producing the same effect by igniting calcined oyster-shells with sulphur; hence this substance was long known under the name of Canton's phosphorus. It is probable that the pure sulphide is not itself phosphorescent, but is rendered so by the presence of traces of other substances. Thus the addition of traces of bismuth and sodium compounds renders the pure sulphide strongly phosphorescent, but not the addition of bismuth compounds alone.[2]

[1] Müller, *Centr. Min.*, 1900, 178.

[2] de Visser, *Rec. trav. chim.*, 1901, **20**, 435; 1903, **22**, 133.

Calcium sulphide is the chief constituent of alkali-makers' waste (p. 301).

Calcium Hydrosulphide, $Ca(SH)_2$, is best obtained by passing sulphuretted hydrogen into a cream of precipitated calcium hydroxide and rather less than four parts of water: it crystallises with $6H_2O$ in colourless prisms, which readily melt in their water of crystallisation.[1] It decomposes when warmed in a stream of sulphuretted hydrogen, yielding calcium sulphide, and is also decomposed by carbon dioxide with evolution of sulphuretted hydrogen and formation of calcium carbonate. It is sometimes used as a depilatory in tan works.

Calcium Hydroxyhydrosulphide, Ca(SH)OH, is obtained by the action of a small quantity of water or of calcium hydroxide on the hydrosulphide,[2] and by the union of water and calcium sulphide, and forms crusts of small, colourless, four-sided needles; it readily dissolves in water, but the solution decomposes rapidly into calcium hydroxide and calcium hydrosulphide, the former separating out as a white precipitate. It combines with carbon disulphide, forming the *basic thiocarbonates*, $Ca(OH)_2,2CaCS_3,7H_2O$ and $2Ca(OH)_2,CaCS_3,10H_2O$, and it appears not unlikely that this substance takes part in the removal of carbon disulphide from coal gas in the lime purifiers (Vol. I., p. 873).

Several other hydroxyhydrosulphides have been prepared, some of which crystallise well, but their constitution is at present doubtful. All these hydrosulphides are oxidised by moist air with formation of calcium sulphite, thiosulphate, or sulphate, and usually with separation of free sulphur.

Calcium Disulphide, CaS_2, is obtained in the form of yellow crystals, containing $3H_2O$, when milk of lime is boiled with excess of sulphur and the filtered solution allowed to cool.

Calcium Pentasulphide, CaS_5, is obtained by boiling calcium sulphide or hydroxide with excess of sulphur for a long time, and forms a reddish-yellow mass, which, if treated with sulphuretted hydrogen in solution, undergoes the reverse reaction, and is converted into calcium hydrosulphide and sulphur.

Calcium Sulphite, $CaSO_3$, is obtained by mixing a solution of a calcium salt with that of a normal sulphite. It forms a white powder which is only soluble to the extent of 0·043 gram in a litre of water at 18°.[3] It is easily soluble in sulphurous acid,

[1] Divers and Shimidzu, *Journ. Chem. Soc.*, 1884, **45**, 270.
[2] Divers and Shimidzu, *loc. cit.*
[3] Weisberg, *Bull. Soc. chim.*, 1896, [3], **15**, 1247.

and if this solution be allowed to stand exposed to the air, six-sided needles separate out which have the composition $CaSO_3,2H_2O$. A solution of this salt in aqueous sulphurous acid, which probably contains *calcium bisulphite*, $Ca(HSO_3)_2$, is met with in commerce, under the name of bisulphite of lime. It is obtained by passing sulphur dioxide into milk of lime, and is used by brewers as a mild antiseptic, and for cleansing and sterilising casks, &c. It is also used in the manufacture of wood pulp and the purification of sugar.

When a nearly neutral solution of calcium bisulphite is electrolysed, *calcium hyposulphite*, CaS_2O_4, crystallises out at the cathode in silky needles, a yield of 30—40 per cent. of the theoretical amount being obtained.[1] This salt is easily

Fig. 127.

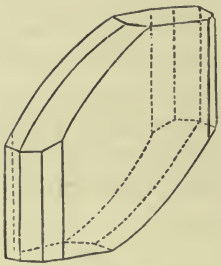


Fig. 128.

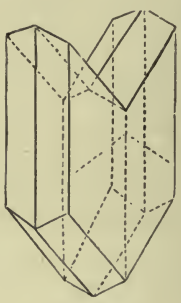


Fig. 129.

oxidised in the air, and has been proposed as a decoloriser and antiseptic for solutions of cane sugar.

Calcium Sulphate, $CaSO_4$, occurs in nature in the anhydrous state in the mineral anhydrite which is often found in limestone rocks, or together with deposits of common salt. More generally, however, the substance occurs as gypsum, $CaSO_4,2H_2O$, found frequently in large monoclinic crystals and known as selenite. The crystalline form of selenite is shown in Figs. 127, 128. The crystals are frequently twinned, and then exhibit the peculiar form shown in Fig. 129. It also occurs as fibrous gypsum or satin-spar, and as crystalline gypsum or alabaster, and has the specific sp. gr. 2·32.

This substance was known from early times as a mineral closely resembling calc-spar, because, like the latter, it became brittle on burning. In 1746 Pott described these two

[1] Elbs and Becker, *Zeit. Elektrochem.*, 1904, **10**, 361; Frank, *Zeit. Elektrochem.*, 1904, **10**, 450.

substances as being different earths, and stated that some chemists assumed that the substance artificially produced by the union of sulphuric acid with lime was gypsum, and termed it *gypsum artefactum*; in 1750 Marggraf showed that these two substances were identical.

Calcium sulphate also forms a hemihydrate, $2CaSO_4,H_2O$, first observed by Johnston [1] as a crystalline deposit in a boiler working at two atmospheres pressure. It is formed when gypsum is heated to 120—130°, and can be prepared pure by heating 20 grams of precipitated gypsum on the water-bath for one hour with 50 c.c. of nitric acid of sp. gr. 1·4, draining and drying. It has the sp. gr. 2·75.

The anhydrous sulphate itself occurs in at least two modifications. Natural anhydrite is almost insoluble in water and the same form can be obtained by heating gypsum strongly. The second modification, which is known as soluble anhydrite, is obtained by completely dehydrating gypsum at 60—90° in a vacuum over phosphoric oxide, and sets with water even more rapidly than the hemihydrate. The relations between these forms, and the temperatures of transition of one into the other are extremely difficult to determine, on account of the slow rate at which the various changes occur, and our knowledge of them is mainly due the elaborate investigations of van't Hoff.[2]

The transition temperatures between gypsum and the other varieties are as follows, the vapour pressure of the system at the temperature of transition being also given:

	Temp.	Vapour pressure.
(1) Gypsum—Natural anhydrite . . .	63·5°	175 mm.
(2) Gypsum—Soluble anhydrite . . .	93°	588 „
(3) Gypsum—Hemihydrate	107°	971 „

These temperatures are considerably lowered by the presence of salts such as sodium chloride, magnesium chloride, &c.

The solubilities of all these modifications and hydrates are also different, soluble anhydrite and the hemihydrate being the most soluble and the natural anhydrite the least soluble. The solubility of natural gypsum according to Hulett and Allen [3] is

[1] *Phil. Mag.*, 1838, **13**, 325.

[2] van't Hoff, Armstrong, Hinrichsen, Weigert, and Just, *Zeit. physikal. Chem.*, 1903, **45**, 257; see also Cameron, *J. Physical Chem.*, 1901, **5**, 556; Moye, *Chem. Zeit.*, 1906, **30**, 544; Cameron and Bell, *J. Amer. Chem. Soc.*, 1906, **28**, 1220.

[3] *J. Amer. Chem. Soc.*, 1902, **24**, 667.

as follows, in grams of $CaSO_4$ per 100 c.c. of solution, a maximum of solubility occuring at 40°; the solubility, however, is greatly affected by the size of the particles which are in contact with the solution:

Temp.	0°	10°	25°	35°	40°
	0·1759	0·1929	0·208	0·2096	0·2097

45°	65·3°	75°	100°
0·2084	0·1932	0·1848	0·162

According to Marignac the solubility of the hemihydrate at 25° is about one part in 100 of water.

In presence of many other salts calcium sulphate dissolves more freely, probably in some cases owing to the formation of double salts. Thus according to Anton 1 part of gypsum dissolves in 122 parts of a saturated solution of sodium chloride.[1] Gypsum is tolerably soluble in boiling hydrochloric acid and in nitric acid, and separates out from the acid solution on cooling in glittering silky needles. When heated with sulphuric acid to 100° it is changed into a porous mass, of which a part dissolves and separates out again on cooling. This consists of microscopic prisms, which have the composition $CaSO_4,H_2SO_4$; it is decomposed by water into its two constituents. Gypsum dissolves very readily in a solution of sodium thiosulphate.

When gypsum is heated at about 120—130°, it loses water and is converted into burnt gypsum or plaster of Paris. This well-known substance when mixed with water combines with it, evolving heat, and subsequently solidifies, taking the form of the vessel in which it is contained. It is therefore largely used for ornamental plaster work, for making plaster casts, and as a cement. It was formerly supposed that the plaster consisted of anhydrous calcium sulphate, and that the setting was brought about by the direct combination of this with two molecules of water, re-forming gypsum, but the researches of Le Chatelier[2] have shown that the properly burnt plaster still contains about 7—8 per cent. of water, and consists of the hemihydrate $2CaSO_4,H_2O$. When this is mixed with water, part of the hydrate, which is much more soluble than either the anhydrous salt or the hydrate with two molecules of water, dissolves in the water to form a

[1] See also Cameron and Brown, *J. Physical Chem.*, 1905, **9**, 210; Sullivan, *J. Amer. Chem. Soc.*, 1905, **27**, 529; Bell and Taber, *J. Physical Chem.*, 1906, **10**, 119.

[2] *Ann. des Mines*, 1887, 345.

saturated solution. This solution, however, is supersaturated with respect to the hydrate $CaSO_4,2H_2O$, and some of the dissolved salt crystallises out in this form, thus allowing the water to dissolve more of the hemihydrate; the same process is then repeated until the whole of the hemihydrate is converted into gypsum. The latter separates in long thin prisms which interlace to form the solid cake which remains. According to Rohland, however, the hardened mass, after setting, must be regarded as a solid solution of the calcium sulphate in water.[1]

If the gypsum be heated too strongly in the burning it only takes up water very slowly and is said to be dead-burnt; this is due to the whole of the water having been driven off, leaving the anhydrous calcium sulphate. Such plaster when exposed to moist air gradually takes up 6—7 per cent. of water, and if then mixed with water it sets slowly, but with a normal hardness.

Another form of the anhydrous sulphate is made by heating gypsum above the temperature of decomposition of the hemihydrate, but below that of the "dead-burnt" sulphate. This is known as hydraulic or Estrich gypsum, and when mixed with water only hardens after an interval of days or weeks. It occurs in pseudomorphs after the hemihydrate, and appears to be intermediate in properties between the soluble and insoluble or "dead-burnt" anhydrite (van't Hoff).[2]

An artificial calcium sulphate is now prepared by precipitating a solution of calcium chloride with dilute sulphuric acid, and is sold under the name of pearl hardening or annaline. It is used by paper-makers as a filling for writing paper. In addition to its employment for plaster work and casts, gypsum is also used as a manure.

Calcium Potassium Sulphate, $CaSO_4,K_2SO_4,H_2O$.—This compound is formed when the solutions of the two salts are mixed together (H. Rose), and occurs as the mineral syngenite. When an intimate mixture of equal weights of the anhydrous salts is stirred up with less than its weight of water, the mass becomes suddenly so solid that it cannot be poured out of the vessel. If four to five parts of water are employed, the solidification takes place somewhat more slowly but still more rapidly than in the case of gypsum alone. Casts made of this mixture possess a polished surface, and are in this respect superior to those made of gypsum.

[1] *Zeit. anorg. Chem.*, 1904, **40**, 182.

[2] Compare Rohland, *Zeit. anorg. Chem.*, 1903, **35**, 194; **36**, 332.

Double salts, $K_2SO_4,2CaSO_4,3H_2O$ and $K_2SO_4,5CaSO_4,H_2O$, are also known.[1]

Calcium Sodium Sulphate, $CaSO_4,Na_2SO_4$, occurs in nature as the mineral glauberite. Sodium sulphate does not act upon plaster of Paris as potassium sulphate does. If, however, a mixture of one part of precipitated calcium sulphate and fifty parts of Glauber's salt be heated to 80° with twenty-five parts of water, a mass of needle-shaped crystals is obtained, which have the formula $CaSO_4,2Na_2SO_4,2H_2O$, and these when further heated are transformed into small crystals of glauberite (Fritzsche).

Calcium Thiosulphate, $CaS_2O_3,6H_2O$, is prepared by heating calcium sulphite with sulphur in water. It forms six-sided triclinic prisms, soluble in their own weight of cold water. When the solution is heated to 60° the salt is decomposed with separation of sulphur. This salt is used in the production of antimony cinnabar, Sb_2OS_2.

Calcium and the Elements of the Nitrogen Group and Boron.

257 *Calcium Nitride*, Ca_3N_2.—Calcium at a dull red heat combines vigorously with nitrogen, forming this compound, the metal becoming incandescent. The preparation is best effected in a nickel tube, the calcium being placed in a nickel boat or dish. The nitride forms brownish-yellow microscopic crystals, and has the sp. gr. 2·63 at 17°. It is decomposed by steam, forming ammonia and calcium hydroxide, and hence this compound supplies a means of converting atmospheric nitrogen into ammonia. It burns when heated in oxygen, and is readily reduced by hydrogen and attacked by the halogens, sulphur, and phosphorus.[2] The formation of this compound is utilised for the isolation of argon from the air (Vol. I., p. 929).

Calcium Nitrate, $Ca(NO_3)_2$.—The alchemist Baldewein, or Balduinus, first prepared this compound whilst searching for a method of absorbing the "Spiritus mundi." He dissolved chalk in nitric acid, and observing that the solid product became rapidly moist on exposure to air, concluded that this substance would prove to be of great power. In the year 1674 he noticed that the solid residue after being heated and then exposed to

[1] van't Hoff, *Sitzungsber. K. Akad. Wiss. Berlin*, 1904, 935; 1905, 305.

[2] Moissan, *Compt. rend.*, 1898. **127**, 497.

sunshine appeared luminous in the dark, and from this time the compound prepared as above was termed Baldwin's phosphorus. Calcium nitrate forms monoclinic crystals containing $4H_2O$, is very deliquescent, and dissolves readily in alcohol as well as in water. The anhydrous salt is a white porous mass, and is often found as an efflorescence on the walls of stables and other places through which urine and other organic liquids percolate. The name lime-saltpetre, or wall-saltpetre, has been given to this salt, which was formerly universally employed for the artificial preparation of nitre.

An amount of this salt corresponding with 17,400 kilos. of nitric acid is now (1912) made daily in Norway by an electrical process from the nitrogen of the air.[1] In the form of a basic salt with lime it acts as an excellent fertiliser.

Calcium Phosphide.—An impure phosphide is prepared by heating lime to a moderate red heat in a Hessian crucible, through the lid of which passes a piece of gas pipe reaching to the bottom, and sufficiently wide to allow of the passage of sticks of phosphorus, which are added in pieces weighing about 15 grams.[2] It forms a very hard, dark mass which is decomposed by water with formation of liquid hydrogen phosphide, P_2H_4, and is employed for the preparation of this substance (Vol I., p. 636). A crystalline phosphide, Ca_3P_2, corresponding in composition with the nitride, is formed when calcium phosphate is reduced by lampblack in the electric furnace, and the amorphous compound is formed when phosphorus vapour is passed over heated calcium. It yields pure phosphine with water, and burns in oxygen at 300°.[3]

Phosphates of Calcium.—The phosphates of calcium are all decomposed by water, the solid residue in contact with the solution being an equilibrium mixture, the composition of which depends on the concentration of phosphoric acid and calcium in the solution. Thus at 25°, the monocalcium and dicalcium salts can exist together in equilibrium with a solution containing 77 grams of CaO and 317 grams of P_2O_5 per litre. With a greater proportion of acid the monocalcium salt alone is stable, with a lower proportion, the dicalcium salt. When the concentration of acid is still further diminished the solid

[1] Witt, *Die Chemische Industrie*, 1905, **28**, 609; Norton, *Utilisation of Atmospheric Nitrogen* (U.S. Dept. Commerce and Labor: Washington, 1912).

[2] Gattermann and Haussknecht, *Ber.*, 1890, **23**, 1176.

[3] Moissan, *Compt. rend.*, 1899, **128**, 787; Renault, *ibid.*, 883.

residue is probably a solid solution of lime and the dicalcium salt.[1]

When the pure salts are treated with water, the dicalcium salt is decomposed to a smaller extent than either the mono- or tri-calcium salt.[2]

Normal Calcium Orthophosphate or *Bone-phosphate*, $Ca_3(PO_4)_2$.—This compound occurs together with calcium fluoride in apatite, $3Ca_3(PO_4)_2,CaF_2$ or $Ca_3(PO_4)_2,Ca_2(PO_4)F$, in which a portion of the fluorine is sometimes replaced by chlorine. Phosphorite and estramadurite are massive varieties of apatite which occur in Estramadura, in Spain. Coprolites, which are found in many sedimentary deposits, and doubtless have an animal origin, consist mainly of calcium orthophosphate. Another pure form of the same compound is the mineral osteolite, and it also occurs as sombrerite, a mineral found on some of the small islands of the Antilles, especially Sombrero, and containing crystals of the mineral ornithite, $Ca_3(PO_4)_2,2H_2O$. Calcium phosphate is also the chief inorganic constituent of bones, forming about 80 per cent. of burnt bones; the other constituents being magnesium phosphate, calcium carbonate, and calcium fluoride.

Pure calcium phosphate is obtained as a white precipitate by adding an excess of common sodium phosphate to an ammoniacal solution of chloride of calcium. It is nearly insoluble in water, but is decomposed by long contact with boiling water into an insoluble basic residue and a soluble acid salt. This decomposition takes place slowly in the cold, and for this reason an exact determination of the solubility of the orthophosphate is impossible.[3] Calcium orthophosphate dissolves readily in water containing ammoniacal salts, sodium nitrate, common salt, and other salts. It is also readily soluble in all acids, even in aqueous carbonic acid. This explains the absorption of the calcium phosphate by the roots of plants; it is then accumulated in the seeds and fruits.

Dihydrogen Dicalcium Orthophosphate, $H_2Ca_2(PO_4)_2$ or $HCaPO_4$.—When a solution of calcium chloride is mixed with one of ordinary sodium phosphate, a white crystalline precipitate of the above compound containing $4H_2O$ is thrown down.

[1] Cameron and Seidell, *J. Amer. Chem. Soc.*, 1905, **27**, 1503; Cameron and Bell, *ibid.*, 1905, **27**, 1512; 1906, **28**, 1222.

[2] Cameron and Seidell, *J. Amer. Chem. Soc.*, 1904, **26**, 1454; see also Rindell, *Compt. rend.*, 1905, **134**, 112; Buch, *Zeit. anory. Chem.*, 1907, **52**, 325.

[3] R. Warington, *Journ. Chem. Soc.*, 1873, **26**, 983.

This compound occurs in urinary concretion, and is sometimes deposited from urine in microscopic crystals grouped in rosettes or stellæ, and known as stellar phosphate. It is scarcely affected by cold water.

Tetra-hydrogen Calcium Phosphate, $H_4Ca(PO_4)_2$.—This salt is obtained in rhombic tablets by dissolving either of the foregoing salts in the requisite quantity of phosphoric acid and allowing the solution to evaporate spontaneously, or by crystallisation at 160° of a solution of calcium carbonate in orthophosphoric acid in which the ratio $P_2O_5 : CaO$ is 4 : 6.[1] If this is treated with cold water it is partially decomposed into the hydrated dicalcium salt, whilst with boiling water the same salt is produced in the anhydrous form (Erlenmeyer).[2]

Superphosphate of Lime.—A mixture of the last mentioned compound and calcium sulphate is manufactured on the large scale, and known in commerce as *superphosphate of lime*. It is usually prepared by acting on bone-ash, coprolites, phosphorites, or other form of mineral phosphate with two-thirds of its weight of sulphuric acid. This mixture is largely employed as a manure, especially for wheat crops. About 727,346 tons of superphosphates were manufactured in Great Britain in 1906, the average value being about £2 10*s.* per ton.

Calcium Ammonium Phosphate, $Ca(NH_4)PO_4,7H_2O$, is precipitated when an ammoniacal solution of ammonium phosphate is added to a solution of calcium chloride in citric acid. It is readily decomposed by water.[3]

Calcium Hypophosphite, $Ca(PO_2H_2)_2$, is used in medicine and is prepared by boiling phosphorus with milk of lime. On evaporating the clear solution, the salt crystallises in bright, six-sided monoclinic prisms.

Calcium Arsenide, Ca_3As_2, corresponds in composition with the phosphide and is obtained in a similar manner. It is a transparent, reddish-brown, crystalline mass of sp. gr. 2·5, and is decomposed by water with production of arsine and calcium hydroxide. When heated in excess of oxygen it burns brilliantly, forming calcium arsenate.[4]

Calcium Boride, CaB_6, is obtained by the reduction of calcium borate with aluminium and carbon in the electric furnace. It

[1] Bassett, *Proc. Chem. Soc.*, 1906, 315.
[2] See also Viard, *Compt. rend.*, 1898, **127**, 178.
[3] Lasne, *Bull. Soc. chim.*, 1902, [3], **27**, 131.
[4] Lebeau, *Compt. rend.*, 1899, **128**, 95.

forms a black powder consisting of transparent microscopic crystals of sp. gr. 2·33, which are sufficiently hard to scratch rubies. It is not affected by water, but is readily attacked by chlorine at a red heat and by many oxidising agents, and burns when strongly heated in the air.[1]

Calcium and Carbon.

258 *Calcium Carbide*, CaC_2.—This compound was obtained by Moissan by heating pure lime and sugar charcoal to a very high temperature in an electric furnace, the following reaction taking place:

$$CaO + 3C = CaC_2 + CO.$$

It is best prepared pure by passing acetylene into liquid ammonia containing metallic calcium [2] and heating the resulting compound, $CaC_2,C_2H_2,4NH_3$, or by the action of acetylene on calcium hydride, the compound CaC_2,C_2H_2, being first formed.[3]

It forms colourless transparent crystals,[4] melts at a higher temperature than platinum, and is decomposed by water with formation of the hydrocarbon acetylene:[5]

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Calcium carbide is formed in small amount during the electrolysis of calcium chloride or fluoride with a carbon cathode. It acts as a strong reducing agent.

Calcium carbide containing about 80 per cent. of the pure substance is manufactured on a very large scale by heating a mixture of limestone with coke or small coal in an electric furnace, the product having a greyish-black appearance. The chief impurities of this material are sulphide, phosphide, and silicide of calcium, the silicides of carbon and iron, and graphite.[6] It is employed for the preparation of acetylene for lighting purposes, the illuminating power of this gas being 12—15 times greater than that of ordinary coal-gas. Theoretically 1 kilo.

[1] Moissan and Williams, *Compt. rend.*, 1897, **125**, 629.
[2] Moissan, *Compt. rend.*, 1898, **127**, 911.
[3] Moissan, *Compt. rend.*, 1903, **136**, 1522.
[4] Moissan, *Compt. rend.*, 1898, **127**, 917.
[5] Moissan, *Compt. rend.*, 1894, **118**, 50.
[6] Le Chatelier, *Bull. Soc. chim.*, 1897, [3], **17**, 793; Moissan, *ibid.*, **21**, 865.

should yield 349 litres of acetylene. The commercial product rarely yields more than 300 litres. Calcium carbide is also used for manufacturing calcium cyanamide (p. 564).

Calcium Carbonate, $CaCO_3$.—This compound occurs widely distributed and in enormous masses in nature, forming whole mountain ranges, being found as limestone of various kinds, marble, calc-spar, and chalk. It also forms the greater part of egg shells, shells of mollusca and coral, and is contained together

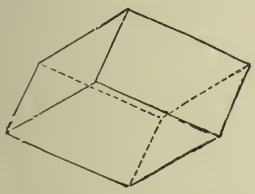


Fig. 130.

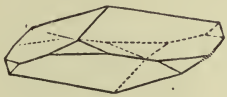


Fig. 131.

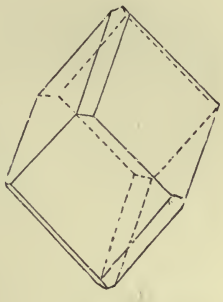


Fig. 132.

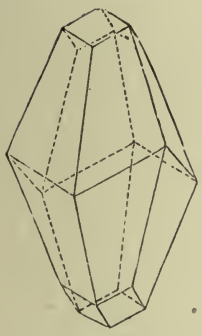


Fig. 133.

Fig. 134.

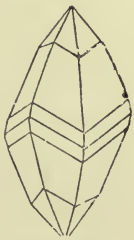


Fig. 135.

with calcium phosphate in burnt bones. Calcium carbonate is dimorphous: it exists in the first place as *calc-spar*, which has a specific gravity varying from 2·70 to 2·75, and crystallises in forms of the hexagonal system (p. 201). Some of the more important of these are seen in Figs. 130—138, a common twin crystal being shown in Fig. 137. The primary form, Fig. 130, is a rhombohedron having angles of 104°5′ and 74°5′. The second form of calcium carbonate is known as *aragonite*, having a specific gravity of from 2·92 to 3·28, and crystallising in the form of rhombic prisms, Fig. 139 (Class 21, p. 201). Another

crystalline form often exhibited by aragonite is that of the penetration twins shown in Fig. 140. A distinction between the two minerals was first drawn by Werner in 1788, and Haüy showed somewhat later that they crystallised in two distinctly different forms. For many years this difference was believed

Fig. 136.

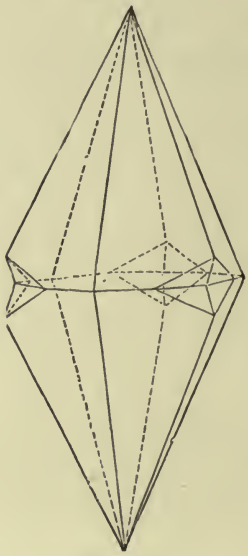


Fig. 137.

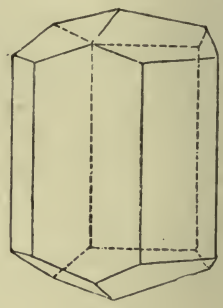


Fig. 138.

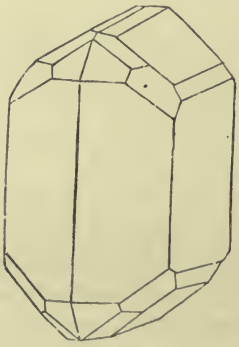


Fig. 139.

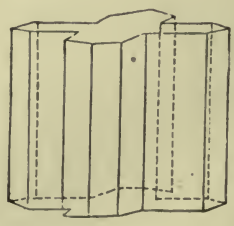


Fig. 140.

to be due to the presence of strontia in aragonite, and it was not until 1819, when Mitscherlich discovered the law of dimorphism, that it was satisfactorily understood.

When a calcium salt is precipitated by the carbonate of an alkali metal, or when carbon dioxide is passed through lime

water, the precipitate which falls down is at first flocculent and amorphous, but gradually becomes crystalline, forming either calcite or aragonite, according to the temperature of precipitation and the nature and concentration of the calcium salt and of the alkali carbonate used.[1] That formed by passing a small quantity of carbon dioxide through cold lime water soon becomes crystalline, the crystals being those of calc-spar, whilst aragonitic crystals are deposited when the lime water is hot (G. Rose). Calc-spar crystals are deposited when a solution of calcium carbonate in carbonic acid is allowed to evaporate spontaneously at the common temperature; but if the solution be heated to 90° aragonite crystals separate out.

Calcite appears to be the more stable form of the two, and the change from aragonite to calcite which occurs at about 470° when aragonite is slowly heated [2] is accompanied by the evolution of a small amount of heat.[3]

One litre of water dissolves 14 milligrams of calcium carbonate at 18°. In presence of free ammonia or ammonium carbonate it is still less soluble. On the other hand, it readily dissolves in water containing carbonic acid in solution, this phenomenon having been first investigated by Cavendish in 1767. The increased solubility in presence of carbon dioxide probably depends on the formation of calcium bicarbonate, $Ca(HCO_3)_2$.

The amount of calcium carbonate dissolved increases with the partial pressure of the carbon dioxide up to a certain maximum, which, according to Treadwell and Reuter,[4] is 1·15 grams of calcium carbonate per litre at 15°. When the partial pressure of the carbon dioxide is zero, the solution at 15° contains 0·385 gram of calcium bicarbonate (0·238 gram of calcium carbonate) per litre, there being no free carbon dioxide in the solution.

When calcium carbonate is heated to about 550° it commences to decompose into quicklime and carbon dioxide, but if the latter is not removed the decomposition is not complete, even if the temperature be raised considerably (p. 129). The pressure of carbon dioxide amounts to one atmosphere at 825°.

When heated to 1400° under a pressure of 30 atmospheres

[1] Adler, *Zeit. angew. Chem.*, 1897, **14**, 431; Meigen, *Chem. Centr.* 1903, II., 1411; 1905, I., 1363; Linck, *Zeit. Kryst. Min.*, 1906, **41**, 633.

[2] Bocke, *Zeit. anorg. Chem.*, 1906, **51**, 244.

[3] Foote, *Zeit. physikal. Chem.*, 1900, **33**, 740.

[4] *Zeit. anorg. Chem.*, 1898, **17**, 170, where the literature of the subject is quoted.

of carbon dioxide the carbonate sinters and partially decomposes but does not melt.[1]

Double Carbonates, $Na_2CO_3,CaCO_3,2H_2O$ and $K_2CO_3,CaCO_3$, have been prepared.[2]

Calcium Cyanamide, CN.NCa.—A crude calcium cyanamide is made by heating calcium carbide in atmospheric nitrogen, or by passing nitrogen over a mixture of lime and carbon at about 2000°.[3] The absorption of nitrogen by the carbide is greatly accelerated by the presence of calcium chloride [4] and similar substances. It forms a black powder and contains about 20 per cent. of nitrogen. This material is used as a fertiliser, the nitrogen becoming available for the plant in the form of ammonia; it is also used for the manufacture of ammonia, cyanides, urea, etc.

Calcium and Silicon.

259 *Calcium Silicide*, $CaSi_2$, was first prepared in an impure state by Wöhler [5] by the action of sodium on fused calcium chloride and silicon, but was obtained pure by Moissan and Dilthey,[6] who heated lime with an excess of silicon in a graphite tube placed in an electric furnace. It forms a crystalline mass of silver-grey colour and metallic lustre, is as hard as quartz, and has the sp. gr. 2·5. It is very slowly attacked by water, with evolution of pure hydrogen, but is rapidly acted on by concentrated hydrochloric acid, hydrogen and silicon hydride being evolved and silicon produced. It can be made to burn in the oxy-hydrogen flame, is decomposed at a red heat by hydrogen chloride and by chlorine, and ignites spontaneously in fluorine.

Silicates of Calcium.—These compounds exist almost in all mineral silicates, certain of these consisting mainly if not altogether of silicates of calcium and isomorphous metals. Among the more important of these are wollastonite, $CaSiO_3$; okenite, $CaH_2Si_2O_6,H_2O$; xonalite, $4CaSiO_3,H_2O$; apophyllite, $4H_2CaSi_2O_6,KF,4H_2O$. Le Chatelier [7] has also prepared

[1] Bocke, *Zeit. anorg. Chem.*, 1906, **50**, 247.

[2] Barre, *Compt. rend.*, 1912, **154**, 279.

[3] German Patent, 150878; *Journ. Chem. Soc.*, 1904, **86**, i., 562.

[4] German Patent, 163320 (Nov. 1, 1901). See also Bredig, *Zeit. Elektrochem.*, 1907, **13**, 69.

[5] *Annalen*, 1863, **125**, 255; **127**, 258.

[6] *Compt. rend.*, 1902, **134**, 503.

[7] *Ann. des Mines*, 1887, 345.

the following anhydrous silicates artificially: $CaSiO_3$, Ca_2SiO_4, $Ca_3Si_2O_7$, and Ca_3SiO_5.

Calcium Sodium Silicate occurs in many localities in Scotland in the mineral pectolite, $4CaO,Na_2O,H_2O,6SiO_2$, which fuses easily to a transparent glass, and is interesting as corresponding most nearly to artificially produced ordinary lime-soda glass.

Calcium Borosilicates occur native as danburite, $CaO,B_2O_3,2SiO_2$, and as datolite, $CaO,B_2O_3,2SiO_2$, both of which melt readily to a clear glass, and are interesting in their relation to the borosilicate glass hereafter described.

HYDRAULIC MORTARS AND CEMENTS.

260 *Hydraulic Mortars.*—When limestone contains about 8 per cent. and upwards of clay, the lime obtained from it yields a mortar which has the property of setting under water and is therefore known as *hydraulic mortar*. Such mortars may also be obtained from "fat" lime by mixing it with certain silicates; thus many Roman buildings are still standing which were constructed with a hydraulic mortar prepared from lime and a volcanic tufa termed *puzzuolana*, found at Puzzuoli, near Naples, and consisting of a mixture of various silicates. This mortar is described both by Pliny and Vitruvius. In place of puzzuolana baked clay and numerous other silicates may be employed.

Cements.—These substances, which differ from hydraulic mortars inasmuch as they do not contain any admixture of free lime, are obtained either by the careful heating of argillaceous limestone, or by calcining a mixture of a suitable clay with the requisite quantity of limestone. *Roman cement*, originally manufactured by James Parker in 1796, was prepared in the former manner, the crude material employed being originally the clay nodules found on the coast of Essex and Kent, termed *septaria*. *Portland cement* is manufactured from limestone and clay, most of the manufacture in this country being carried out in the valley of the Medway, the river mud of which is very suitable for the purpose. The limestone and clay are ground together, and the mixture, termed "slip" or "slurry," after drying is carefully burnt in a kiln; the fuel employed is coke, alternate layers of the mixture and fuel being placed in the kiln. The carbon dioxide is thus completely eliminated, and the lime

produced combines with the clay, forming chiefly calcium silicate and aluminate. The cement clinker drawn from the kiln is broken up and then ground between millstones. The following analyses of English (1 and 2) and German (3 and 4) Portland cements give the composition of the material :—

	1.	2.	3.	4.
Lime	59·06	55·06	62·81	57·83
Silica	24·07	22·92	23·22	23·81
Alumina	6·92	8·00	5·27	9·38
Ferric oxide . .	3·41	5·46	2·00	5·22
Magnesia . . .	0·82	0·77	1·14	1·35
Potash	0·73	1·13	1·27	0·59
Soda	0·87	1·70		0·71
Calcium sulphate	2·85	1·75	1·30	1·11
Clay	1·47	2·27	2·54	—
Sand				

When the powder is mixed with water to a paste it heats somewhat, and the mixture if left at rest stiffens in a few hours and continues to harden, becoming solid within a day, and gaining considerable strength within a week; it does not however, attain its full hardness for many months. Nothing further than water is required for the setting, and the water is all absorbed; the cement will consequently set in a closed space or under water, and therefore goes by the name of Hydraulic Cement. It is much stronger than ordinary mortar, and is chemically a different body. The cement is used for making large blocks widely employed for engineering and building works, for constructing water-tight tanks and chemical plant, and for making thin porous diaphragms for the electrolytic preparation of the alkalis.

The Setting of Cements.—The cause of the setting of cements has been the subject of much discussion; the explanations formerly given were very incomplete, but the researches of Le Chatelier[1] have thrown considerable light on the subject. He examined the action of polarised light on the crystalline substances which can be observed under the microscope in Portland cement, and compared these optical properties with those of a number of calcium silicates and aluminates which he prepared artificially. From these experiments he concluded that the chief constituents of cement are tricalcium orthosilicate,

[1] *Annales des Mines*, 1887, 345.

$3CaO,SiO_2$; tricalcium aluminate, $3CaO,Al_2O_3$,; and tricalcium aluminoferrite, $3CaO,2(Al,Fe)_2O_3$, properly made cement containing no free lime. On the other hand S. B. and W. B. Newberry [1] consider that the essential constituents of the cement are the tricalcium silicate and dicalcium aluminate. On the addition of water, the calcium compounds are decomposed with formation at first of free calcium hydroxide, and there are then formed crystalline hydrated calcium silicate and aluminate, the crystals of which form an interlaced mass, thus bringing about the setting of the cement. The setting takes place long before the formation of the hydrated crystals is complete, and as the action goes on the cement becomes continuously harder. There is therefore no such difference between the setting and hardening actions as in the case of ordinary mortar.

GLASS.

261 Ordinary glass consists essentially of a mixture of the silicates of calcium and of the alkalis, although for special purposes the calcium silicates may be wholly or partly replaced by numerous other silicates, and phosphoric and boric acids may be in part substituted for silicic acid. The subject of the composition and manufacture of glass may therefore be conveniently considered here.

Glass differs from the simple silicates of which it is composed, inasmuch as it is almost insoluble in water and acids. It fuses at a high temperature, and on cooling passes through all stages of viscosity until the solid state is reached, and whilst in the plastic condition can not only be shaped and cut, but may also be readily welded, the gentlest contact serving to effect a permanent junction. As glass may be varied in composition by imperceptible degrees, it is clear that it is not composed of single substances in a vitreous condition like fused silica, SiO_2, or fused boric anhydride, B_2O_3, but of a mixture of various substances such as $CaO,Na_2O,6SiO_2$ with Na_2SiO_3, or $CaSiO_3$ and SiO_2, forming together a complex solution the components of which have so feeble a rate of crystallisation that when cooled no separation takes place from the melt, which gradually becomes vitreous and solid, so that

[1] *J. Soc. Chem. Ind.*, 1897, **16**, 887.

no definite solidifying or melting point is observed. Certain kinds of glass, however, contain components which have a quicker rate of crystallisation, and when these components separate the glass is said to devitrify.

Historical.—The manufacture of glass appears to have been discovered by the Egyptians, although the ancients themselves attributed the discovery of glass-making to the Phœnicians. Glass vessels of various sizes, both colourless and coloured, have been found in Egyptian tombs which belong to an age prior to that in which the Phœnicians occupied themselves with glass-making. Indeed, the latter nation appear rather to have been engaged in exporting the glass made in Egypt, and especially at Thebes, into different parts of the ancient world, than to have established any original manufacture of their own. In the tombs of Beni Hassan near Thebes, which were built more than 2000 years B.C., we find paintings representing Egyptians carrying on the processes of glass-blowing. From these, as well as from the glass vessels which are found in the tombs, it appears that the Egyptians were not only acquainted with the art of glass-making and of working in glass, but likewise with that of cutting and colouring glass, by which they imitated precious stones. Thus an urn has been found made of white glass and ornamented with patterns in white and in light- and dark-blue glass showing the ring of Thoutmosis, who reigned in the 17th century B.C. Specimens illustrating all the stages of the process of glass-making, and dating from about 1400 B.C., have been found at Tell el Amarna.[1]

Aristophanes is the first Greek author who mentions glass (ὕᾶλος), *i.e.* a drop of rain, and in his *Clouds* he refers to a glass lens which was used as a burning-glass. Amongst Latin authors, Cicero is the first to mention Egyptian glass, and we find that at the time of Augustus the Egyptian glass was highly valued in Rome, so much so that when this emperor subdued Egypt (29 B.C.), a portion of the tribute was ordered to be paid in glass; this material afterwards being so highly valued by the Romans that Aurelius levied an import duty upon it.

Glass works were established in Italy, France, and Spain at

[1] For further information see Sir Gardner Wilkinson, *The Manners and Customs of the Ancient Egyptians*, vol. iii., p. 88, edit., 1837; and *Tell el Amarna*, by W. M. F. Petrie (London, 1894).

an early date. These glass-houses, however, only manufactured common objects for everyday use, and it was not until after the introduction of Egyptian workmen to Rome that artistic glass-ware was made in Europe. This took place during the reign of Tiberius, and the art made such rapid progress that in the time of Nero, Roman glass rivalled in every respect the original Egyptian manufacture. According to Pliny, Egyptian soda and sand were employed in the manufacture of glass, and he remarks that in India rock-crystal was used for this purpose, and that in his time the material which was most highly valued for making glass was that which approached most nearly to this mineral. Manganese was used as a decolorising agent and the materials employed to produce coloured glasses were identical with those which are at present in use.

After the fall of the Western Empire the glass manufacture followed Constantine to Byzantium, and for five centuries the Eastern capital became a renowned seat of the glass manufacture. On the decay of the Empire of the East, the glass-makers wandered to various parts of Europe, many being attracted to the Venetian Republic. Here glass-making greatly flourished. As a protection against fire, it is said, the manufacture of glass was removed in the year 1289 from the city of Venice to the adjacent island of Murano, and here during the 16th and 17th centuries the Venetian glass manufacture attained its highest development, the elaborate productions of Venetian art becoming famous throughout the civilised world. No fewer than 8,000 men were, it is stated, employed at that time in the manufacture, and so important did this branch of Venetian trade become, that strict laws were promulgated to prevent the secrets of glass-making from becoming known to foreign workmen, the supervision of the glass-houses being confided to the chief of the Council of Ten. The Venetian glass industry received, however, a check in the 17th century, from which it has recovered only in recent years.

In the early Middle Ages an independent manufacture of glass arose in Germany, and glass-painting is entirely of German origin ; the manufacture of glass mirrors appears also to be a German invention. At first the glass was coated with a plate of metal, and it was not until the 15th century that the present process was introduced. In addition to table-glass and window-glass, artificial gems, glass rings, and other objects of art were manufactured in Germany. Agricola, in his treatise *De re*

Metallica, published in the year 1530, gives the first drawing of the interior construction of a glass-furnace, and in this work as well as in Mathesius' *Sarepta or Bergpostill* (1564), we find explicit and interesting directions concerning the manufacture of glass as carried on in Venice, Germany, and Bohemia. In the last-named country the glass industry began to flourish in the 16th century, the purity of the quartz found there enabling manufacturers to produce the colourless glass for which the Bohemian glass-houses have long been famous and in which they still excel. When the Venetian glass manufacture fell into decay, Bohemian glass replaced Venetian, but in time the Bohemian manufacture again suffered a relapse, owing to the heavy import duties which were levied upon glass-wares as well as to the fact that other governments held out inducements to the Bohemian workmen to settle in foreign countries; like the Venetian manufacture, it is only in recent years that the Bohemian glass industry has recovered its original position.

In the meantime many of the German princes patronised the glass-makers, and each became celebrated for some peculiar manufacture. Thus a glass-house at Potsdam was well known for its manufacture of ruby glass. This glass-house was established under the direction of Joh. Kunkel, and in 1685 he published the first edition of his *Ars Vitraria Experimentalis*, in which he gave a translation of the collection of receipts published at Florence by Antonius Neri in 1612, and added to them remarks of his own and those of E. Merret.

Glass-works were also set up in France at an early date, but it was not until the 18th century, when workmen were introduced from Germany, that a pure kind of French glass-ware was made. De Nehou in 1688 erected a glass-works at Paris; this was afterwards removed to St. Gobain, where it soon became and still remains the most important plate-glass works in the world.

The first manufacture of glass of which we hear in England is that of window-glass established in the 15th century. The product cannot, however, have been very good, for in an old deed made in 1439 by the Countess of Warwick and a glazier of Westminster named Prudde, it is distinctly stipulated that no English window-glass is to be used. In the reign of Elizabeth, French artists were brought to London, and these carried on their trade of making window-glass at Crutched Friars in 1557, whilst flint-glass was first manufactured at a

glass-house at Savoy House in the Strand. Mirror-glass, used for looking-glasses, coach-windows and similar purposes, was first manufactured in England at Lambeth by Venetian workmen brought over in 1670 by the Duke of Buckingham. The first large plate-glass works were established in 1771 at St. Helens under the name of the Ravenshead or the British Plate-glass Company, and this company continues to flourish up to the present time.

The glass industry was introduced into Russia in the 17th and 18th centuries by German and Bohemian workmen. In the United States the same manufacture appears to have been established by Robert Hewes, a citizen of Boston, who erected a glass-house in the forest which existed in New Hampshire. The manufacture of Hewes does not seem to have been successful, and in 1800 another attempt was made to establish a glass-house at Boston, which also failed, until a German of the name of Lint took charge of the works in 1803, and the State of Massachusetts agreed to pay a bounty on all glass manufactured by him.

262 *The Materials used in Glass Manufacture.*—Silica is used in the forms of quartz, ignited flints, white sand, and ordinary sand. Potash is used in the form of purified potashes. Soda was used, in the form of the native carbonate, trona, by the Egyptians, and in the form of artificial carbonate made from kelp by the early European glass-makers until 1831, when the cheaper soda ash made by the Leblanc process was used. More recently the soda has been added in the form of sulphate. Laxmann in 1764 tried to use the native sodium sulphate from Siberian salt-lakes, and in 1803 Baader succeeded in employing salt-cake made as in the Leblanc soda process; and when in 1856 Pélouze found a method of obtaining salt-cake practically free from iron, the use of salt-cake became almost general. Only the soda of the sodium sulphate mixes and combines with the other glass materials, as carbon is specially added to reduce the sulphuric anhydride, and the gaseous products thus formed escape with the furnace gases; no practicable process has been suggested by which the sulphur compounds can be condensed and utilised. Lime is used in the form of calc-spar, marble, chalk, or limestone. Lead is used as red lead, white lead, and litharge.

It is almost impossible to obtain materials perfectly free from iron, and as ferrous oxide, even in small quantities, imparts to

glass a deep green tint, whereas ferric oxide gives to the glass a light yellow colour, scarcely visible when present in small quantities, and carbon imparts to the glass a deep yellow or brown tint, a decolorising agent is generally added with the object of oxidising the iron and the carbon; for this purpose manganese dioxide (pyrolusite), arsenious oxide, or saltpetre is used in the manufacture of lime glass, whilst red lead is employed in the manufacture of flint glass.

263 *Composition of Glass.*—The several kinds of glass commonly met with may be roughly divided according to their composition into four chief varieties:

I. Soda-lime glass; II. Potash-lime glass; III. Potash-soda-lime-iron glass, whose composition is regulated mainly by the cheapness of the raw materials available; and IV. Potash-lead glass. The following table shows the composition of these kinds of glass:

	SiO_2.	K_2O.	Na_2O.	CaO.	PbO.	$(Al,Fe)_2O_3$.
I.	71–78	0–2	12–17	5–15	—	1–4
II.	72–76	12–15	0–3	8–10	—	1
III.	60–65	3–5		18–20	—	6–11
IV.	40–50	8–11	—	—	38–53	1

I. *Soda-lime Glass* is remarkable for the comparatively low temperature at which it fuses and the consequent ease with which it can be worked, and also by its cheapness, while it can be obtained as clear and colourless as the more expensive kinds of glass. Owing to the ease with which it may be blown, welded and otherwise worked with simple sources of heat, it is used for making glass tubes and laboratory apparatus. On the large scale it is employed as window-glass and plate-glass, and is then known as crown glass. Its specific gravity varies from 2·4 to 2·6, and its refractive index is about 1·530 for the D line.

II. *Potash-lime glass,* or *Bohemian glass,* possesses a high fusing point and requires a high temperature to work it; it is less acted upon by solvents than the other kinds of glass. The above properties fit it especially for the manufacture of chemical apparatus, and in particular for combustion tubes.

III. *Common* or *bottle glass* is distinguished by its yellow, brown, or green colour, due to the iron and other impurities present in the cheap raw materials used, such as common

coloured sand, basalt, wood ashes, the residual alkaline and lime-salts from alkali works, gas works, and soap works, common salt, salt-cake, clay and rocks containing felspar. The iron silicate being comparatively easily fusible allows of the diminution of the more costly alkali silicates. This glass is more difficultly fusible than soda-lime glass, and is also more readily attacked by acids.

IV. *Potash-lead glass, Flint glass, Crystal* or *Strass* is distinguished by being very fusible and easily worked, although the heating must be done in an atmosphere free from reducing gases, as these reduce the lead silicate to metallic lead, thus making the glass opaque and black. The glass has a higher specific gravity, viz., 3·0—3·8, brighter lustre, and greater refractive power, viz., 1·70—1·78 for the D line, than any of the preceding kinds of glass. *Crystal* contains an extra proportion of lead and is used for optical purposes, whilst *strass* contains a still larger proportion; these are distinguished by high refractive indices and great lustre. Lead glass is more easily attacked by aqueous solutions than the preceding kinds, and is therefore not suitable for chemical apparatus, although it is sufficiently resistant for the manufacture of many articles in common use, especially table glass.

Special glass of unusual composition.—Besides potash-soda-lime-lead glass, many kinds of glass are made in which magnesium, zinc, barium, antimony, arsenic, aluminium, lithium, didymium, thallium, iron, and manganese oxides replace partially or even completely the first-named oxides, and in which the silica is partially replaced by boric and phosphoric oxides. Boro-silicate glass containing zinc and barium oxides is remarkably resistant to the action of water and is known as Jena glass. Another boro-silicate glass is used for high temperature thermometers. Many different glasses are used for optical purposes, their mean refractive index varying from 1·49 for a boro-silicate lime glass to 1·65 for a lead-barium silicate glass, their dispersion C—F varying from 0·007 to 0·020. Phosphate-silicate glass containing alkali, alumina, and baryta is used for microscopic objectives, and a remarkable glass consisting of a boro-silicate of barium, zinc, and aluminium, and entirely free from alkalis, is used for photographic objectives. Other kinds of glass particularly transparent to the ultra-violet rays are used for astronomical objectives, and special electric glow lamps. On the other hand a dark green glass containing ferrous oxide

is quite opaque to radiant heat. Glass of particular shades of red, green, and blue-violet are used in colour photography, and glass of other shades is employed for isochromatic monotone photographs and for photographing microscopic objects after the use of particular stains. Lastly, glass of pure fused silica must be mentioned, articles of which are now manufactured on a considerable scale and are found very valuable in the laboratory and in technology, *e.g.*, in the concentration of sulphuric acid. (See Vol. I., p. 914).

264 *Thermal Expansion of Glass.*—The necessity for annealing glass and the mode of preparation of toughened glass alike depend on the thermal expansion of the glass. A very interesting case of a glass nearly free from thermal expansion is found in quartz glass obtained by fusing pure quartz in the oxy-hydrogen flame or electric furnace, and drawing, welding, and blowing the vitreous melt into the required forms. Such quartz glass vessels may be dropped white hot into cold water without cracking, *i.e.*, will withstand a sudden temperature change of over 1000°. The coefficient of expansion of quartz glass per 1° C. is 0·00000052. Jena or resistance glass, now extensively used for making glass laboratory vessels, will withstand temperature shocks of 190° C., while Bohemian glass, having a higher thermal expansion, will barely stand shocks of 95° C. The thermal expansion of a glass depends upon its chemical composition and may be calculated from the percentage composition by multiplying each percentage by the following factors and summing the products ;[1] the factors are :

B_2O_3	0·000,000,003
SiO_2	027
ZnO	060
P_2O_5	066
BaO	100
PbO	100
CaO	166
K_2O	283
Na_2O	333

An example of a special glass with a very low expansion coefficient, viz., 0·0000045, is the particular glass used for incandescent gas lamps.

[1] See Hovestadt, *Jenaer Glas* (Gustav Fischer, Jena, 1900).

For the manufacture of thermometers it is of great importance that the glass shall regain its original volume as rapidly as possible after it has undergone a change of temperature. Special glass for this purpose is now made under the name of Jena normal-glass which has the following composition:

B_2O_3	SiO_2	Na_2O	ZnO	CaO	Al_2O_3	Mn_2O_3	Total
2·0	67·3	14·0	7·0	7·0	2·5	0·2	100·0

After being heated to 100° thermometers of this glass only show a depression of the zero of 0·06°, whilst ordinary thermometers show depressions of from 0·4 to 1·0°.[1]

A further improvement is effected by enclosing within the thermometer bulb a small rod of another kind of glass having the same coefficient of expansion, but a much larger thermal after-effect, when the depression of the zero is corrected.[2] The importance of mercurial thermometers reading reliably at high temperatures has led to the introduction of instruments filled above the mercury with nitrogen, and the pressure exerted by this on the bulb has necessitated the use of glass of very high melting point. By careful attention to the composition of such glasses, the range of thermometers has been gradually extended from 360° up to 450°, 550°, and in 1898 even 575°.

The Manufacture of Glass.

265 The materials employed for the manufacture of the glass are first fritted together in melting pots. These pots require great care in their preparation and are made of the most refractory kind of fire-clay, such as that found at Stourbridge. When charcoal or gas is used as fuel the pots are open (Fig. 141); when, however, coal is employed, and especially in flint-glass making, the pots are hooded or covered at the top, having a mouth in front like a muffle as seen in Fig. 142. The melting-furnace is built of sandstone, or of moulded blocks made of the purest fire-clay. The construction of the oldest form of glass-furnace, as used in the time of Agricola, is shown in Fig. 143. It is hemispherical and is heated by a wood fire placed in the lowest opening; the second opening gives access to the melting-pot, whilst the upper space serves as the annealing oven. The small

[1] *Zeit. Instrumentenkunde*, 1883, **3**, 377; 1891, **11**, 330; 1892, **12**, 402.
[2] Schott, *Zeit. anal. Chem.*, 1898, **37**, 585.

Bohemian furnace, in which wood is employed as a fuel, shown in Fig. 144, was formerly common in Germany. The older glass-houses were usually built in the form of a truncated cone, open at the top, from 60 to 80 feet in height, and from 40 to 50 feet in diameter at the base, the centre of the area being used for the melting-furnace, capable of holding from 5 to 10 glass-

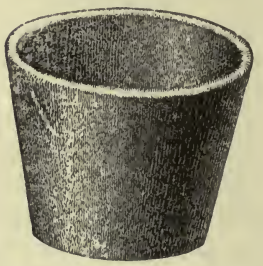


Fig. 141.

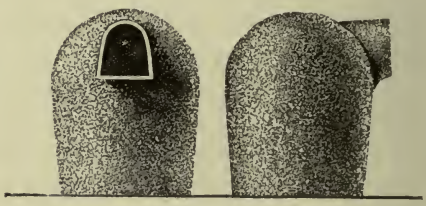


Fig. 142.

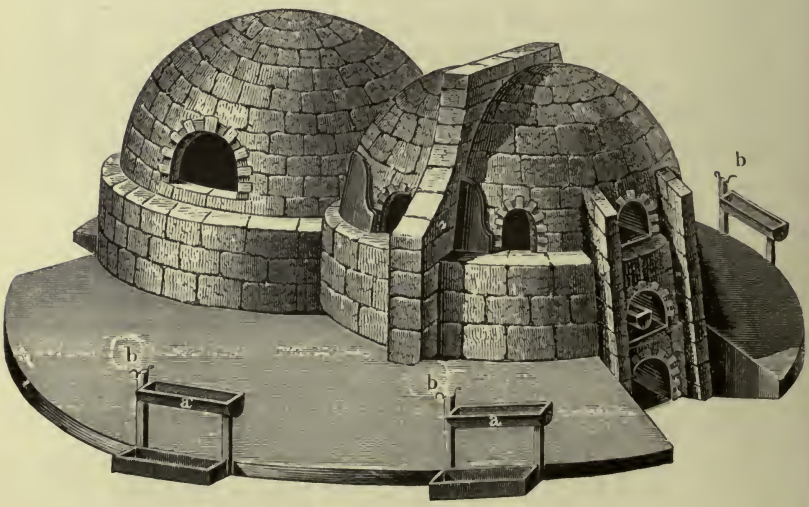


Fig. 143.

pots or crucibles for melting the materials. The wood used in early times as fuel was gradually replaced by coal, and this change necessitated an alteration in the form of the furnace. In order to insure complete combustion, and to bring about a sufficiently high temperature when the fuel used is coal, the arrangement shown in Fig. 145 is made use of, the whole of the furnace being enclosed in a conical chimney.

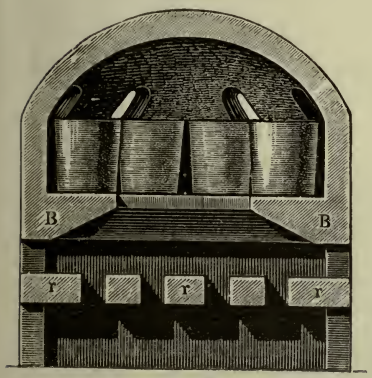


FIG. 144.

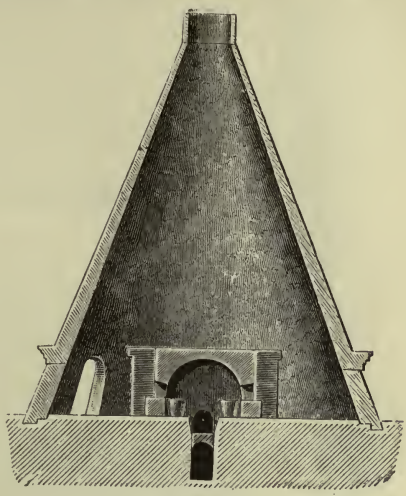


FIG. 145.

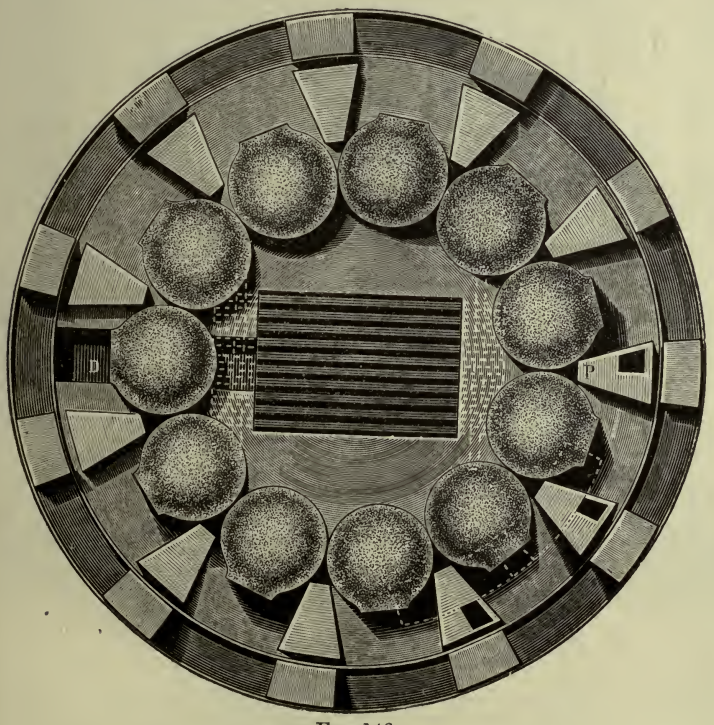


FIG. 146.

Figs. 146 and 147 show the construction of a modern English flint-glass furnace in plan and in vertical section. Ten

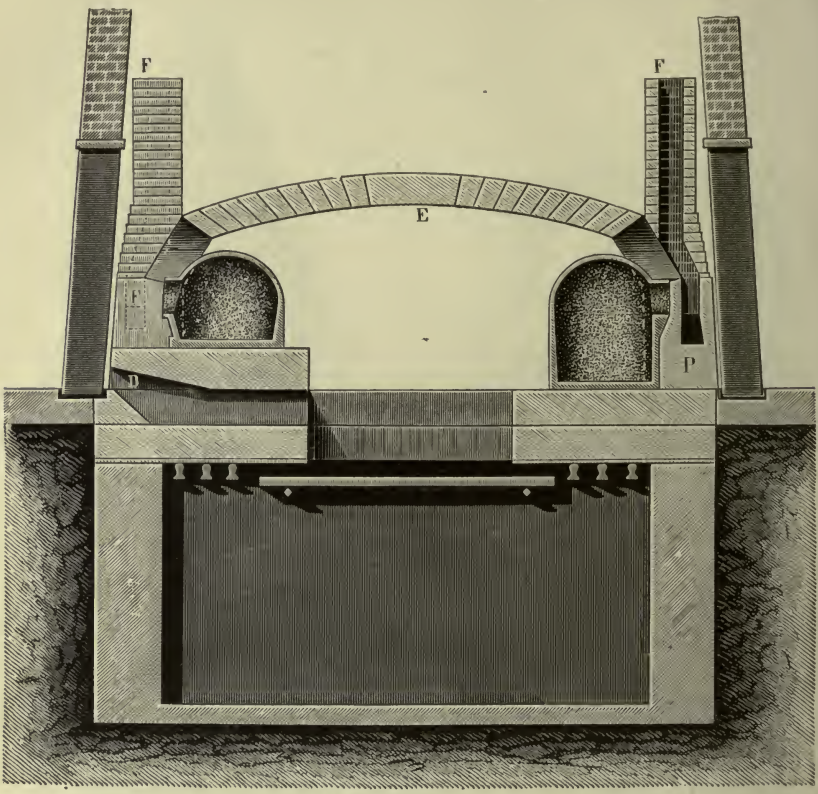


FIG. 147.

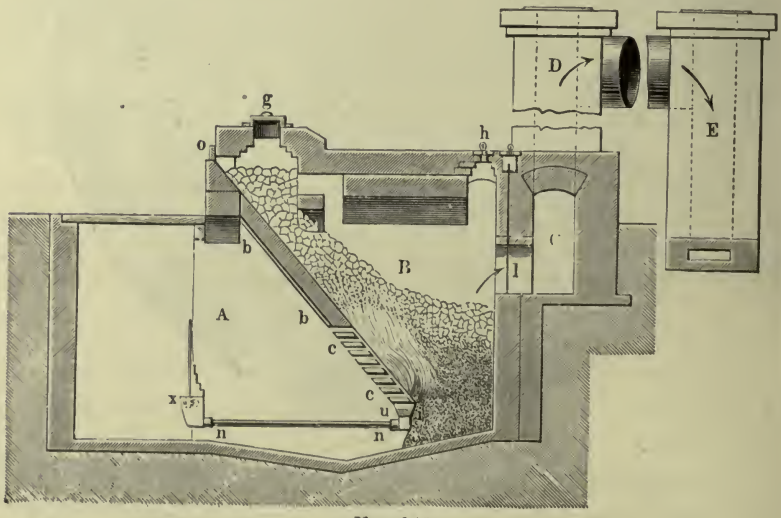


FIG 148.

large glass-pots are placed round the walls of the furnace, with their mouths towards the outside, opposite corresponding holes in the external wall of the furnace, so that the molten glass can be readily withdrawn. A small pot is placed above the firing-

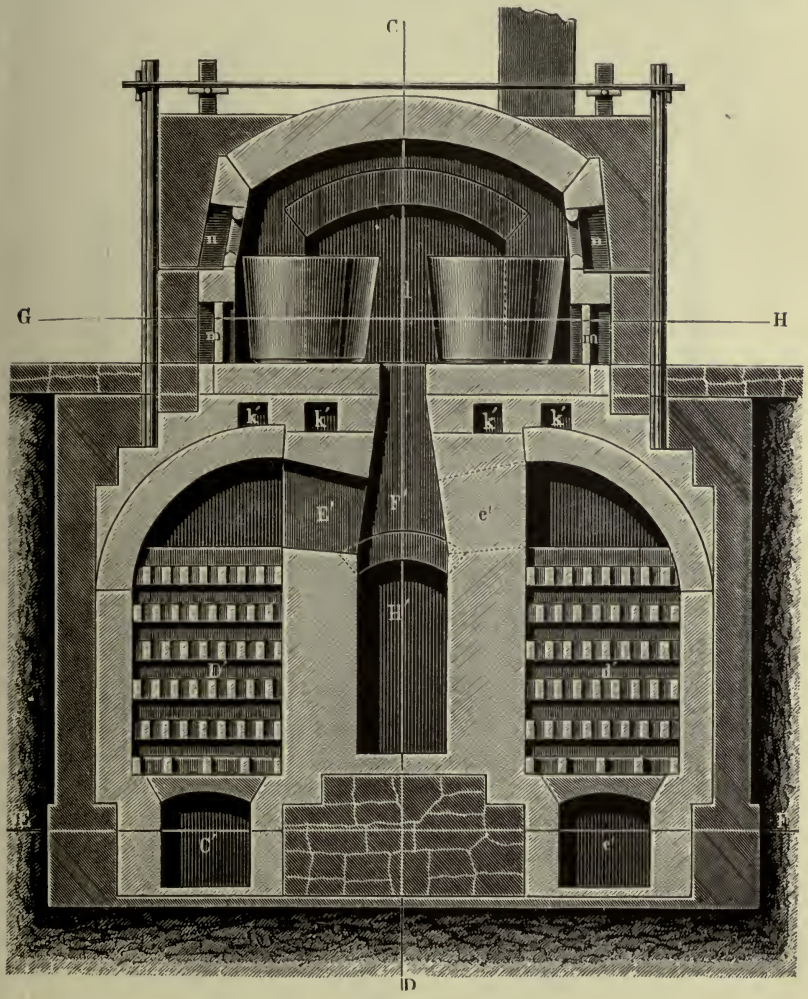


Fig. 149.

hole D. The grate for the coal fire is situated in the centre of the furnace and the flames striking on the arch or crown E (Fig. 147) play round each pot and find their way through the flues (F) in the pillars into the common chimney.

Amongst modern glass-furnaces that invented by Siemens is

the most successful. Fig. 148 shows the gas generator, which is situated at some distance from the melting-furnace. In this the coal falls down through the opening (g) on to the inclined plane (bb), whence it passes on to the bars (cc) of the furnace. Here an incomplete combustion takes place and the coal lying

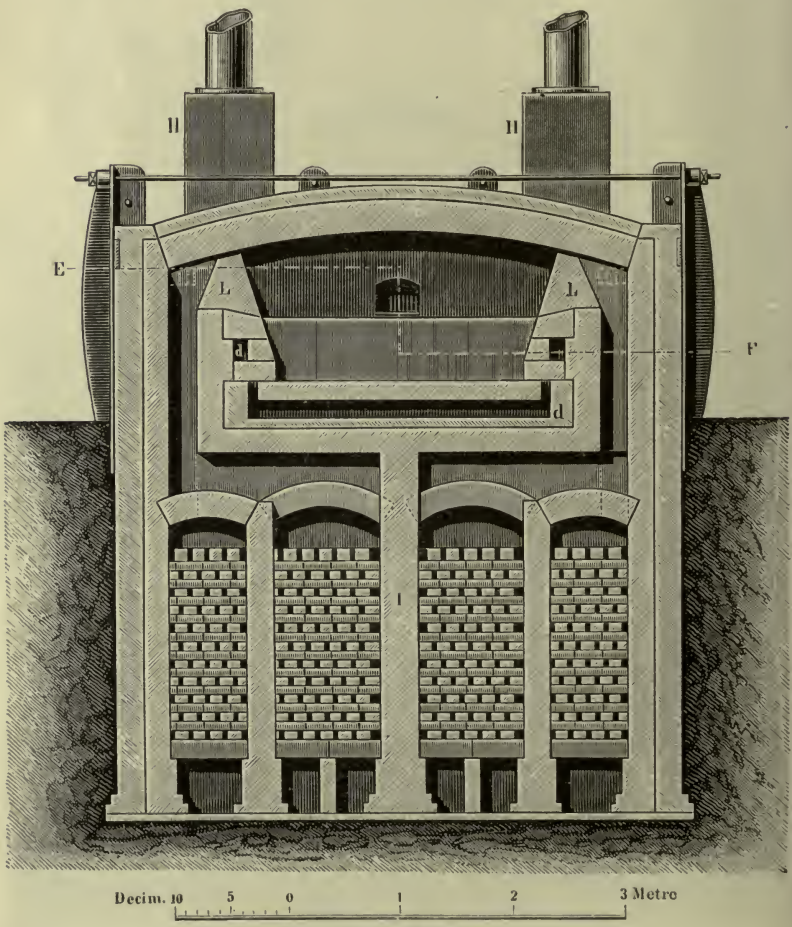


Fig. 150.

above the grate undergoes dry distillation; the gases pass through the flues (C) (D) and (E), and are led into the melting-furnace, the construction of which is seen in Fig. 149. Here the gas passes at first through the flue (C′) to the regenerator (D′), where it is heated, and thence passes by the flues (E′ F′) into the furnace, whilst the air necessary for the combustion of

the gas is allowed to enter through the air passages; the products of combustion pass from the furnace by a flue not

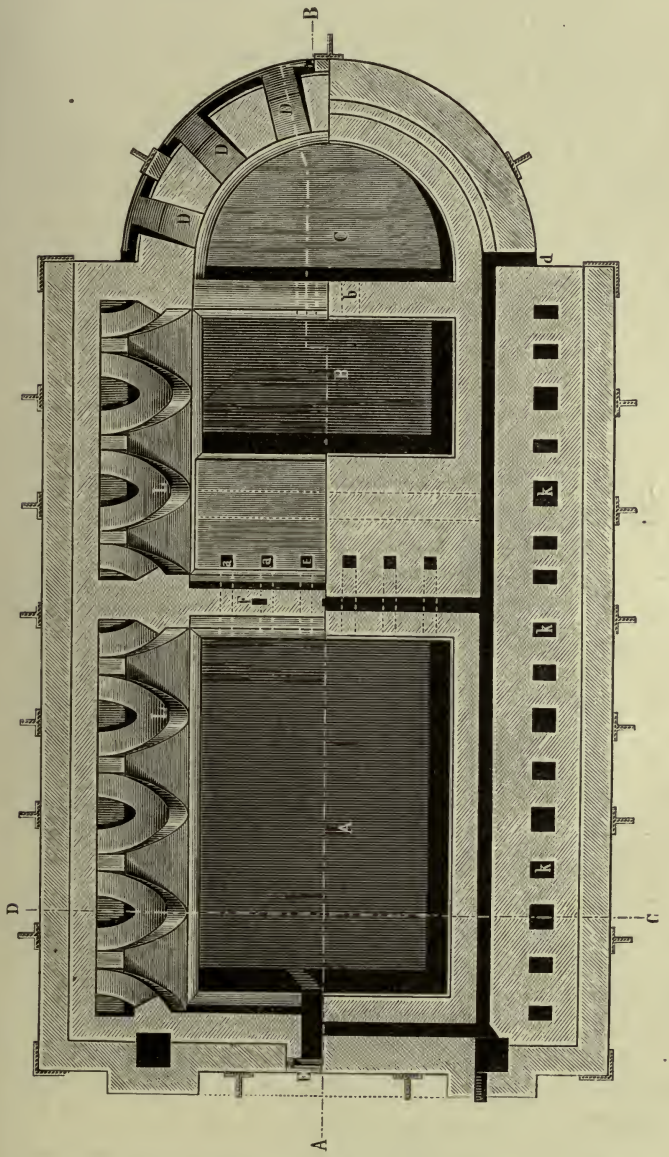


Fig. 151.

shown, but placed behind (F′) and thence by the flue (e′) to the second regenerator (d′) and so to the flue (c′) and to the chimney. After about twenty minutes the regeneratór (D′) has

cooled, while the regenerator (d′) has been heated to a fairly high temperature, and by now altering the position of large valves in the several flues, the direction of the gas is reversed, so that it is heated on its way to the furnace by the regenerator (d′), while the waste gases from the furnace impart a portion of their heat to the regenerator (D′).

Fig. 150 shows a vertical cross section, Fig. 151 a horizontal section, and Fig. 152 a vertical longitudinal section of an improved form of a Siemens glass-melting furnace. This furnace resembles the one last described, in having the regenerative arrangement for recovering the waste heat as shown at (D′d′) Fig. 149, but is remarkable for an improved method of construction and mode of working, the glass being placed in *tanks* instead of in *pots*. In the older forms of glass-furnace the materials are first charged into the glass-pots, then fritted and melted down and worked out completely, after which the pots are re-charged and the process repeated. Hence a considerable loss of time and waste of fuel take place through the intermittent nature of the work. Siemens' improvement has for its object the rendering of the process of glass-making a continuous and more uniform one. It consists of an arrangement of tanks (A), (B), (C), Fig. 152 of which (A) serves to receive the raw materials; in this tank they are fritted together and afterwards fused. From (A) the liquid "metal" flows into (B), the clarifying compartment, whence it passes into (C), the working compartment, from which it can be withdrawn by the workmen in the usual manner through the doors (D, D). The compartment (A) is fed with raw materials through the charge-aperture (E) at the back of the furnace. This compartment (A) is separated from the tank (B) by a division wall (F), Fig. 151, in which a series of passages is formed, one of which is seen at (a a) Fig. 152. Through these passages the melted glass flows, and from (B) it passes to the tank (C) through the passages (b) in the division wall (G). The sides and bottom of the tank are honeycombed with air-passages (d d d), through which cold air is caused to circulate by the draught produced in the chimney (H), and thus the tank walls are maintained in a cool condition so as to enable them better to withstand any injurious action of the melted glass. The gas-ports are shown at (k k), and the heated air issues from corresponding openings passing in diverse directions over the upper edges of the wall. By this means an effectual intermixture of the combustible gas and the heated air is produced, and the

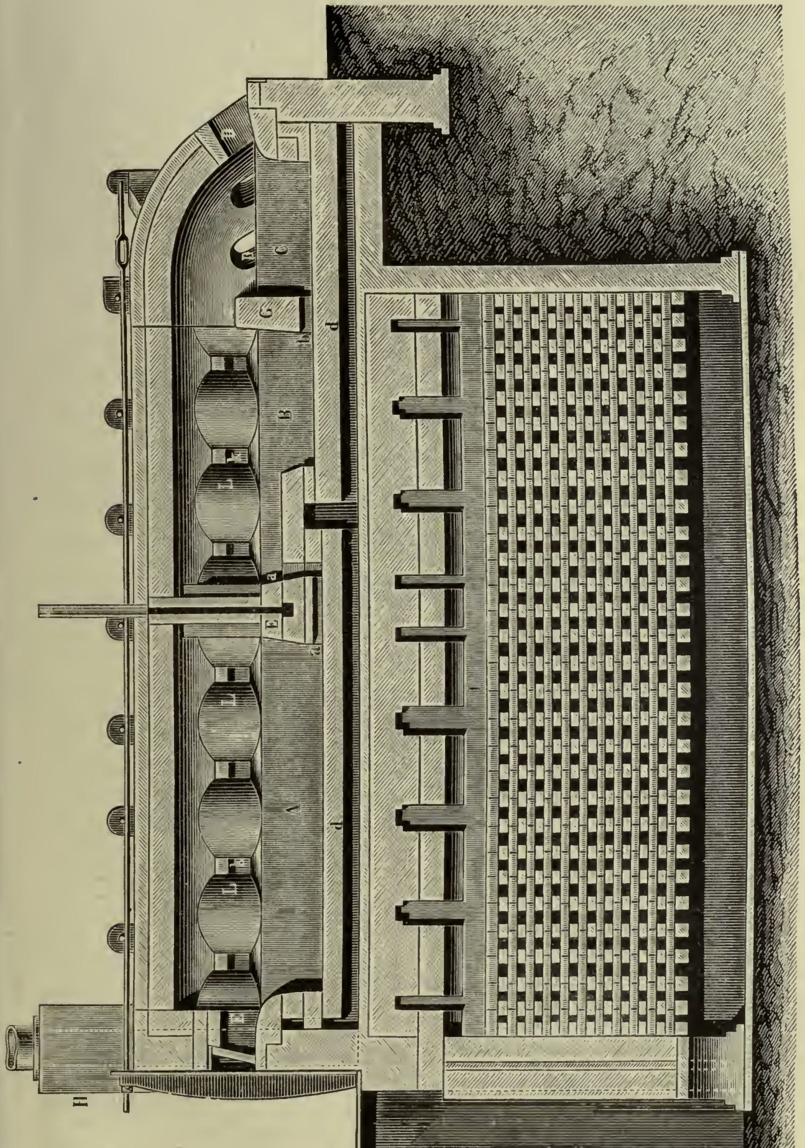


FIG. 152.

air is prevented from coming into immediate contact with the surface of the melted glass in the tanks. By arranging the gas- and air-ports along the sides of the tanks, the temperature in the different parts of the furnace can be regulated according to the various stages of the preparation of the glass in the several compartments.

The materials required for the formation of the glass are, if possible, always mixed with broken glass of the same kind, technically termed "cullett," for the purpose of increasing the fusibility of the mass. The materials, however, are not placed in the pots until these are heated up to a high temperature. The furnace is kept very hot until the first portion of the material added has been fused, and then a second portion is introduced. When all the solid matter is dissolved, the glass is still full of small bubbles of gas, and is of a spongy nature and not yet in a fit state for working. Moreover, the surface of the melted mass is covered by a layer of salts chiefly consisting of chlorides and sulphates of potassium and sodium which have escaped perfect vitrification; this is termed *glass-gall* or *sandiver*. Formerly, when impure materials were more generally employed than is now the case, large quantities of this scum were formed. Now, however, its formation is avoided by the use of purer materials and by the addition of charcoal if salt-cake is employed, care being taken not to add an excess, as otherwise the glass assumes a yellow colour. The last process in glass-making is termed the "fining," and consists in the removal by subsidence of the heavier non-vitrified particles, and the escape of the bubbles of gas to the surface. For this purpose the glass must be brought into as liquid a state as possible, and consequently at this stage of the operation the temperature is raised to the highest point. When all the gas-bubbles and the glass-gall have disappeared, the temperature of the furnace is allowed to fall slowly, the object being to reduce the fluidity of the glass to the point at which it becomes viscid and in a workable condition. Glass is worked either by the skill of the glass-blower, for the production of the ordinary hollow- or blown-glass articles, or by casting in presses, or, lastly, by pouring the "metal" out on to iron tables and rolling it into plates. The tools described by Blancourt in his work *On the Art of Glass*, printed in London in 1699, are almost the same as those now in use.

It should be mentioned that oil firing is now being used to some extent, a mixture of air and oil being sprayed into the furnace

Annealing.—All articles made of glass require to be very slowly and homogeneously cooled, for those portions of the glass which are on the outside solidify first, and leave the interior portions still warm, and these, unable to contract on cooling, are left in a state of tension; hence glass which has been quickly cooled cracks and falls to pieces with the slightest disturbance, such as is caused by a very slight scratch. All glass therefore requires to go through the *annealing* process. This consists in submitting the glass articles to a very slow cooling. The construction of an annealing oven is shown in Fig. 153.

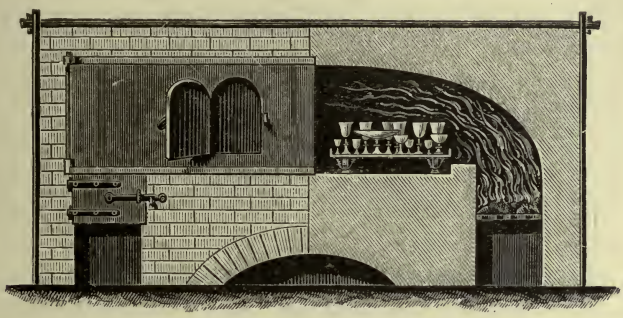


Fig. 153.

The fact of the brittleness of glass when suddenly cooled is well seen in the so-called *Rupert's Drops* (Fig. 154), obtained by allowing a little melted glass to fall drop by drop into cold water. By merely breaking off the thin point the whole mass

Fig. 154.

is converted with a slight detonation into a fine powder. Similarly an ordinary thick tumbler made of unannealed glass flies to pieces when the slightest scratch is made on the interior surface, as when a small piece of flint is allowed to fall into the glass.

Toughened glass is a particular kind of strained and partly annealed glass, discovered by De la Bastie. The glass articles, heated almost to redness, are suddenly immersed in oil heated to 300°, and are then allowed to cool gradually, or sheets of

glass are allowed to cool between plates of suitably heated metal. The glass thus prepared is able to withstand sudden changes of temperature better than the untoughened glass; it is also not readily broken when dropped, but when by increasing the severity of the blow it is broken, it falls into fine splinters. Although a crack may occur in the vessel of toughened glass without the whole mass breaking up, yet it cannot be cut with a diamond, and the plates have accordingly to be made of the size ultimately required.

Laboratory Glass Working.—The methods of constructing special pieces of apparatus, though they cannot be here described, are of considerable importance to the research chemist, and to those engaged in the examination of any gaseous products; assistance in acquiring this art may be obtained from special manuals on the subject.[1]

266 *Decomposition of Glass.*—It is of especial importance for the chemist that his glass vessels should satisfactorily withstand the action of chemical reagents. Bernard Palissy, Lavoisier, and Scheele were well aware of the solvent action of water upon glass, and they explained this by the solution of the alkaline silicates, whilst the insoluble silica or lime silicate floated about in the liquid. In his celebrated researches on the atomic weights of the elements, Stas [2] describes a series of preliminary experiments made for the purpose of ascertaining the kind of glass which is least subject to such deterioration. He found that glass containing lead or alumina was readily acted upon by acids, whilst potash-lime glass withstood this action best, and he prepared a glass of the following composition, which was sufficiently capable of resisting solvents and at the same time fusible enough to enable it to be worked into the various forms of chemical apparatus :

SiO_2	K_2O	Na_2O	CaO
77·0	7·7	5·0	10·3 = 100

Emmerling [3] found the solvent action of boiling solutions on glass vessels to be within certain limits proportional to the time during which the action takes place, and naturally it is also proportional to the surface exposed to the action

[1] *The Methods of Glass Blowing*, Shenstone, 1886; *Glass-Blowing and Working*, Bolas, 1898.

[2] *Nouvelles Recherches, &c., Mem. Acad. Belg.*, **35**, 216.

[3] *Annalen*, 1869, **150**, 257.

of the liquid. Dilute alkalis attack glass very much more rapidly than neutral or acid solutions, and hence it follows that in order to diminish the errors which occur in quantitative analysis from the solvent action of reagents upon glass, the long continued contact of alkaline liquids must especially be avoided, any such liquid being acidified before evaporation; it is also advisable to avoid the use of new glass vessels, which are attacked much more rapidly than old ones. It appears that the most resistant glasses have approximately the molecular composition 8·6 SiO_2 : 1 CaO : 1·2 $(Na_2,K_2)O$, the relative proportion of soda to potash making little difference.[1]

The number of milligrams of glass destroyed per hour on an exposed surface of one square decimetre by various solutions is given approximately by the following figures, the glass being such as is used for making flasks, beakers, &c., and known as (1) Bohemian glass, (2) Jena glass. Water at 20°, (1) 0·0040, (2) 0·0002; water at 80°, (1) 0·50, (2) 0·02; sulphuric acid 5 per cent. at 100°, (1) 1·7, (2) 0·0; sodium carbonate 10 per cent. at 100°, (1) 20·0, (2) 8·0; sodium hydroxide 8 per cent. at 100°, (1) 15·0, (2) 17·0.

Glass is slowly attacked by the moisture and the carbon dioxide contained in the air, so that the surface gradually becomes spotted with minute crystals of sodium carbonate or with minute drops of potassium carbonate solution, and this action is accelerated in hot saturated air. Badly prepared window glass, especially that rich in alkalis, becomes opaque in the course of time. This is due to a similar decomposition of the surface, so that the carbonates of the alkalis being washed away, an iridescent coating consisting of a thin film of calcium silicate remains. This iridescence is especially well seen in antique glass which has been buried in the earth for a considerable length of time. A similar iridescent surface is now produced artificially by heating ordinary glass under pressure in contact with hydrochloric acid. Borosilicate glasses, and especially those containing zinc and barium, are particularly permanent on exposure to the air. The decomposition of the surface of glass is often not to be seen until the glass is heated, when the surface dehydrates and cracks.

Devitrification of Glass. Réaumur's Porcelain.—In 1739, Réaumur observed that if a piece of glass were surrounded by

[1] Weber and Sauer, *Ber.*, 1892, **25**, 70; Mylius and Foerster, *ibid.*, 1889, **22**, 1092; 1892, **25**, 97.

sand or gypsum, and heated strongly for a considerable length of time it was converted into a porcelain-like mass, to which he gave the name of *porcélaine par dévitrification*. According to the experiments of Pélouze, Benrath,[1] and Stolba,[2] the porcelain-like glass possesses the same composition as ordinary transparent glass. Devitrification results from the gradual precipitation or crystallisation of certain ingredients of the vitreous solution, and the liability to devitrify depends on the composition of the glass.

Opaque, Coloured and Matt Glass.

267 *Milk-glass.*—The ordinary opalescent or milk-glass is either soda-glass or flint-glass which has been rendered opaque by the addition of an insoluble powder, such as bone-phosphate or mineral-phosphate.

Enamel.—Another opaque variety of glass is known under the name of *enamel*. This name originally signified lead-glass rendered white by oxide of tin, but oxide of antimony and sulphate of barium are now also employed. Enamel is used for covering the surface, or for "enamelling" iron vessels used for cooking and for chemical manufacturing purposes. Enamels may be coloured by any of the materials next described for colouring glass, such coloured enamels being used for making ornaments by fluxing them on to plates or articles of gold or copper, to which they readily adhere.

Ruby Glass.—The older chemists were acquainted with the fact that glass could be coloured a ruby-red tint by means of various gold compounds. Thus Neri describes a method of preparing ruby glass by adding to the glass-maker's materials the residue from the evaporation of a solution of gold in aqua regia. General attention, however, was drawn to this subject in the 17th century, after the discovery of the *purple of Cassius*, obtained as a dark-red powder by mixing the chlorides of gold and tin (p. 508). Amongst other chemists, Kunkel occupied himself with the preparation of this gold pigment, and obtained from the Elector Frederic William the sum of 1,600 ducats for his experiments.

In his *Ars Vitriaria Experimentalis* he says: "There was a certain *Doctor medicinae*, by name Cassius, who discovered the

[1] *Die Glasfabrication*, 1875, 18.
[2] *J. pr. Chem.*, 1863, **90**, 465; 1864, **93**, 118.

præcipitatio Solis cum Jove: to this perhaps Glauber may have given occasion, but I leave this undecided. The aforesaid Doctor Cassius endeavoured to bring it into glass, but when he tried to form a glass with it, or when he took it out of the fire it was as colourless as crystal, and he could not bring any permanent red out of it. He may, however, have observed, being a man curious about these things, amongst the glass-blowers that when they softened glass in the flame of the lamp the colour underwent a change. Thus he came to try the same plan with gold glass, and obtained a splendid ruby colour. When I learnt this, I set to work at once, and I know best what trouble I had to hit the proper composition, and to find out how to get it always red."

The secret which is involved in the above words is explained in the *Laboratorium Chymicum*, which appeared after his death: "This ruby glass possesses the property that when the glass is melted with the ☉ (gold) it comes out of the fire as clear as crystal, and in order to become red must be heated again in a mild fire."

On the addition of purple of Cassius or of gold chloride, to a melt of glass, the latter remains perfectly colourless when quickly cooled; but when reheated to the point at which it becomes soft, the whole mass attains a ruby-red colour. By the addition of tin or silver compounds, a variety of tints between a rose-red colour and a red-purple colour can be obtained. It is probable that the colour is due to metallic gold in so finely-divided a state that the substance only allows red light to pass through it; indeed, the presence of fine particles of gold in ruby glass has recently been detected by the ultramicroscope.[1] The amount of gold contained in ruby glass is very small, amounting to from 0·05 to 0·06 per cent.

Cuprous oxide also colours glass a fine and intense red, but inasmuch as this compound readily undergoes oxidation and as cupric oxide imparts to glass a light green colour, a reducing agent such as iron scale is added to the materials. Oxidation is also prevented by poling the molten mass with pieces of fresh wood. The glass on cooling appears of a light green colour, but becomes red on re-heating. The preparation of this glass was also understood in early times. Klaproth found both copper and iron in a sample of old Roman glass, and in the beginning of

[1] Zsigmondy, *Zeit. physikal. Chem.*, 1906, **56**, 65; see also Garnett, *Proc. Roy. Soc.*, 1905, **76**, A, 370.

the 17th century, Neri described a method of calcining copper in order to colour glass, and stated that iron filings, iron scale, or other reducing agents must be added in order that the colour might come out a bright red. Kunkel also employed himself with the preparation of this glass, but in later times the art was lost, and it was not until the year 1828 that Engelhardt examined the question and obtained a prize which the Berlin Polytechnic Society had offered for the discovery, since which time the method has been generally practised. Cuprous oxide possesses a very strong colouring power, and for this reason copper-ruby is generally flashed on to colourless glass, as otherwise the colour would be altogether too intense. The glass blower brings the requisite quantity of colourless glass on to his blowpipe, and dips this into the molten coloured glass so as to cover the former with a thin film, and the compound glass is then blown and shaped in the usual way. By examining the cut edge of a piece of flashed copper ruby glass the thin layer of coloured glass resting on a very much thicker layer of colourless glass is distinctly visible. By grinding or etching through the flashed colour highly decorative effects may be obtained; this art of flashing and grinding was known to the ancients, as is shown by the celebrated Portland Vase made of black glass flashed over with a milk white glass.

Ferric oxide (colcothar) also imparts a red colour to glass, but the tint is less brilliant than either of the two just described.

Yellow Glass is prepared by the addition of potassium antimonate or of antimony-glass (a fused and imperfectly oxidised sulphide of antimony); other yellow colours are obtained by the use of silver chloride and silver borate. Organic bodies also impart a yellow tint to glass. This must have been observed by Thomas Aquinas, who describes a mode of preparation of artificial topaz by placing a piece of aloe-wood over the vessel in which the glass is melted. It was formerly believed that this brown colour was due to carbon. Splitgerbe has, however, shown that it is caused by the presence of the sulphides of the alkali metals obtained by reduction from the sulphates contained in the material used for glass-making.

Green Glass is obtained by the addition of cupric oxide, as was known to the ancients, the above substance being found in antique glass. According to Seneca, Democritus of Abdera was acquainted with a method for producing the emerald artificially, and Theophrastus, about 300 B.C., described a mode

of colouring glass green by means of copper. Other green tints are obtained by the addition of oxide of chromium and ferrous oxide, the latter giving a dull bottle-green colour.

Blue Glass.—Cobalt oxide colours glass a fine *blue*, and this oxide has been used from early times for this purpose.

Violet Glass.—The *violet* colour of glass is obtained by the addition of black oxide of manganese and nitre.

Black Glass.—A fine *black* opaque glass is obtained by the addition of sesquioxide of iridium to colourless glass, and a common black glass is prepared by adding large quantities of ferric oxide, with which copper oxide or cobalt oxide is frequently mixed.

Paste.—The property of glass to attain a variety of tints by the addition of various metallic oxides is made use of for the production of imitation gems or paste, and this art has now attained such perfection that it is difficult even for an adept to ascertain upon mere inspection of a stone whether it is genuine or only an imitation. Strass is employed for the basis of paste, because of its high refractive power and bright lustre. According to Donault-Wieland *topaz* is formed by adding to 1,000 parts of strass, 40 parts of antimony-glass and 1 part of purple of Cassius. *Ruby* is obtained from the ingredients of the topaz mixture by fusing 1 part of this with 8 parts of strass and allowing the fused mass to remain at the temperature of the furnace for thirty hours. *Emerald* is prepared by fusing 1000 parts of strass, 8 parts of cupric oxide, and 0·25 part of chromium oxide. *Sapphire* can be made by the addition of 15 parts of cobalt oxide to 1,000 of strass; *amethyst* requires the addition of 8 parts of manganese dioxide, 5 of cobalt oxide, and 2 of purple of Cassius; whereas *beryl* or *aqua-marine* is prepared by adding 7 of antimony-glass and 0·4 of cobalt oxide to the 1,000 of strass, and *Syrian garnet* or *carbuncle* requires 500 of antimony-glass and 4 parts each of manganese dioxide and purple of Cassius to the same quantity of strass. These special tints can, however, be readily varied at pleasure.

Avanturine Glass has received its name from a rare form of quartz which occurs in Spain and the Altai, containing spangles of mica or other mineral. Avanturine glass is more beautiful than the natural mineral, and the method of its manufacture is said to have been discovered by chance in the 13th century by Briani in Venice. The artificial avanturine was largely employed for the preparation of ornaments and especially for Venetian mosaic work. The details of

its preparation were long kept secret, and the process was only carried out by a few of the highest Venetian families. In the year 1847 Pettenkofer[1] investigated the preparation of the antique hæmatine, an opaque red glass, and in the preparation of this material he obtained by accident avanturine glass. Many not wholly successful attempts have been made to determine the exact conditions under which the avanturine is thus formed. Avanturine glass is a white soda-lime glass, containing an excess of alkali, coloured red by cuprous oxide and containing an enormous number of minute spangles of metallic copper, probably produced by the partial decomposition of cuprous silicate.[2] According to Hautefeuille, a green cupric glass is first prepared; to this iron filings are gradually added until it becomes red and opaque; hæmatine glass is thus formed, which is then well covered with ashes, and allowed gradually to cool, when the artificial avanturine glass is formed.

Matt Glass.—The etching of glass with hydrofluoric acid was known in the 17th century, but it is only recently that this process has been employed for the decoration of glass, and now etched glass is much used in place of the more expensive cut-glass. Gaseous hydrofluoric acid as well as many soluble fluorides produce a dull or matt surface on glass possessing also a considerable degree of opacity, but liquid hydrofluoric acid produces, according to the concentration of the acid, a more or less transparent matt-surface. According to Tessié de Mothay and Maréchal, the best mode of obtaining opaque-etching by means of hydrofluoric acid is to employ a bath made of 1,000 parts of water, 250 parts of crystallised double fluoride of hydrogen and potassium, 250 parts of commercial hydrochloric acid, and 140 parts of potassium sulphate. This last salt renders the fluorides of calcium and lead which may be formed less soluble, whereby they are separated out in the crystalline form on the portions of the glass which have been etched and thus tend to render the surface more opaque.

The matt-surface is now usually produced on glass by exposing it to a sand blast, the parts which are to remain smooth being protected by paper. Reagent bottles may readily be indelibly labelled in this manner. The matt-surface on whole sheets of glass is obtained by grinding with sand.

Quartz Glass and Fused Silica Ware.—The fact that quartz can

[1] *Dingl. Polyt. Journ.*, 1847, **145**, 122.
[2] Auger, *Compt. rend.*, 1907, **144**, 422.

be easily fused in the electric furnace and worked up into articles for chemical use is referred to in Vol. I., p. 914. Such articles are now manufactured both in this country and abroad, white sand or selected quartz being fused, and made into tubes, rods, muffles, flasks, &c., the value of which for chemical research can hardly be overestimated.

Detection and Estimation of Calcium.

268 The fact that certain compounds of calcium impart a red colour to the flame of the spirit-lamp was first observed by Ribbentrop in 1796. The spectrum of a non-luminous gas flame tinted by calcium chloride exhibits a number of lines, of which the green line Caβ is the most characteristic, the orange line Caα being also very prominent (see Fig. 21, p. 154). This spectrum is mainly due to the chloride and oxide and not to the vapour of the metal itself, and is also yielded by calcium compounds which do not volatilise in the flame, when they are moistened with hydrochloric acid and placed on a platinum wire in the hottest portion of the flame. Certain silicates containing calcium which are not decomposed by hydrochloric acid must be first heated with ammonium fluoride, the residue then decomposed by sulphuric acid, and treated as above. By means of the spectroscope as small a quantity as 0·00006 of a mgrm. of calcium chloride or similar salt may be detected. At the temperature of the electric arc the calcium compounds show the spectrum of metallic calcium, consisting of a number of fine bright lines.

Calcium may be separated from the alkali metals by the addition of a solution of ammonium carbonate, calcium carbonate being precipitated. As has been stated, this latter salt is not altogether insoluble in water, and it is, therefore, preferable to precipitate the lime as calcium oxalate by the addition of ammonium oxalate in neutral or ammoniacal solution; this salt is slightly soluble in water (0·0068 g. per litre at 25°), but much less soluble in dilute ammonium oxalate solution, which is therefore used instead of water for washing the precipitate. This reaction is usually employed for the estimation of calcium; the washed and dried precipitate, which has the composition $CaC_2O_4,2H_2O$, is either gently ignited, by which means it is converted into the carbonate; or it is strongly ignited, when the carbonate is converted into caustic lime. The amount of

oxalate may also be ascertained volumetrically by treating the precipitate with dilute sulphuric acid and titrating with potassium permanganate. Calcium is also occasionally estimated as the sulphate. The precipitation by sulphuric acid must, however, be made in presence of alcohol, and the precipitate must also be washed with the same liquid.

The Atomic Weight of calcium was first accurately determined by Erdmann and Marchand,[1] by the ignition of calc-spar and of precipitated calcium carbonate. From their experiments it appears that the atomic weight of calcium is 39·68, 39·70, 39·73, or as a mean of the three numbers 39·7 (pp. 10, 11). Baup[2] obtained the number 39·67 as the result of the analysis of organic lime salts. Hinrichsen,[3] by the careful ignition of calc-spar, has obtained the number 40·14 (O = 16), and Richards,[4] by the analysis of the chloride, found 40·13. The most probable value is now (1913) taken as 40·07.

STRONTIUM. Sr = 87·63.

269 The name of this element is derived from that of Strontian, a village in Argyllshire, in which a peculiar mineral, strontium carbonate or strontianite, was originally found. At first this mineral was mistaken for barium carbonate, but in the year 1790 Crawford suggested that it contained a peculiar earth, founding his opinion upon experiments which had been made on the mineral by Cruikshank. This was confirmed in 1792 by Hope,[5] and independently by Klaproth,[6] a year afterwards. Sir Humphry Davy in 1807 first obtained the metal strontium.

Strontium occurs chiefly as the sulphate or *celestine*, $SrSO_4$, and as the carbonate or *strontianite*, $SrCO_3$. Many specimens of aragonite and of calc-spar contain small quantities of strontium carbonate; and the same may be said of many kinds of limestone, marble, chalk, and other rocks,[7] and also many iron

[1] *Annalen*, 1844, **52**, 210; 1848, **66**, 219.
[2] *Annalen*, 1844, **52**, 212.
[3] *Zeit. physikal. Chem.*, 1901, **39**, 311; 1902, **40**, 746.
[4] *J. Amer. Chem. Soc.*, 1902, **24**, 374.
[5] Account of a mineral from Strontian, *Trans. Roy. Soc. Edinb.*, 1792, **4**, 3.
[6] *Crell. Ann.*, 1793, **2**, 189, and 1794, **1**, 99.
[7] Hillebrand, *J. Amer. Chem. Soc.*, 1894, **16**, 81.

ores and other minerals,[1] although the strontium is generally present only in very small traces. *Baryto-celestine* is a mineral which contains the sulphates of barium and strontium, and the latter compound occurs also in small quantities in different varieties of heavy spar. Strontium occurs as a silicate in *brewsterite*, $H_4(Ba,Sr,Ca)Al_2Si_6O_{18},3H_2O$. Small quantities of the chloride and sulphate of strontium occur in solution in many brine-springs as well as in different mineral waters. It is also present in chalk waters, such as that of the London basin, and has been found in plants, being in some cases derived from the calcareous fertilisers which have been applied to the soil. Strontium has also been found in sea-water in the ashes of *Fucus vesiculosus* and in the spicules of certain radiolaria (Bütschli).

Preparation of Metallic Strontium.—Davy obtained the metal strontium by the electrolysis of either the moistened hydroxide or the chloride. It was afterwards prepared by Bunsen and Matthiessen,[2] who electrolysed a fused mixture of strontium chloride and ammonium chloride, using a thin iron wire as cathode, and obtained the metal in pieces weighing half a gram or less. The metal prepared by them was yellow and probably contained nitride. It has been obtained in a pure condition by Borchers and Stockem by the application of the method which they had employed successfully for the preparation of calcium (p. 531).

It has also been prepared indirectly from strontium amalgam, but the metal obtained by simply heating the amalgam does not appear to be pure. Strontium amalgam can be obtained by heating a saturated solution of strontium chloride to 90° with 20 per cent. sodium amalgam,[3] but is more conveniently prepared by electrolysing a solution of strontium chloride with a mercury cathode, washing the product with water, pressing between folds of filter paper and then heating to 150°.[4]

In order to prepare pure strontium, the amalgam containing 8 per cent. of strontium is heated in vacuo to 700°, and then to about 1000° in hydrogen. The mercury is thus completely removed and a compact mass of the hydride obtained. This is then heated in small quantities in vacuo in an iron tube con-

[1] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533, 547.
[2] *Journ. Chem. Soc.*, 1856, 107.
[3] Franz, *J. pr. Chem.*, 1869, **107**, 253.
[4] Guntz and Roederer, *Bull. Soc. chim.*, 1906, (3), **35**, 494.

tained in a porcelain tube. The hydride decomposes, and the strontium volatilises and is condensed on a polished hollow steel tube, cooled by a stream of water. The metal thus obtained contains 98·6—99 per cent. of strontium, and may be obtained still less impure (99·4 per cent. Sr) by redistillation in vacuo.[1] Glascock has prepared it from the fused chloride.[2] Pure strontium is a crystalline, silver-white metal of sp. gr. about 2·5; it has the same hardness as lead, melts at about 800°, and volatilises freely at 950°. It very rapidly loses its lustre in the air and takes fire when simply rubbed with a hard body, whilst the finely-divided metal inflames spontaneously in the air, forming a mixture of oxide and nitride. The metal burns with a dazzling red flame when heated in oxygen, and is also readily attacked by the halogens, hydrogen chloride, sulphur, hydrogen sulphide, phosphorus, &c. It decomposes water and alcohol, and is readily dissolved by acids (Guntz and Roederer). It is less electro-positive than calcium and the alkali metals. Strontium behaves towards liquid ammonia like the alkali metals (p. 379).[3]

STRONTIUM COMPOUNDS.

270 The preparation of strontium compounds free from calcium and barium is a matter of considerable difficulty. It is not easy to effect a separation of isomorphous salts, hence calcium and strontium cannot be separated by means of their chlorides, nor strontium and barium by means of their nitrates. The purification is best accomplished by dissolving the crude carbonate in hydrochloric acid, precipitating foreign metals by strontium oxide, followed by chlorine water, and then precipitating most of the barium by the addition of concentrated hydrochloric acid. Sulphuric acid is then added, and the greater portion of the mixed sulphates converted into carbonate by ammonium carbonate. The precipitate is next dissolved in dilute nitric acid and fractionally precipitated with sulphuric acid until no barium is contained in the precipitate. Calcium is removed from the nitrate by repeated precipitation of the strontium nitrate by alcohol.[4]

[1] *Compt. rend.*, 1906, **142**, 400; *Bull. Soc. chim.*, 1906, (3), **35**, 503; also *Compt. rend.*, 1910, **151**, 813.

[2] *J. Amer. Chem. Soc.*, 1910, **32**, 1222.

[3] See also Roederer, *Bull. Soc. chim.*, 1906, (3), **35**, 715.

[4] Sörensen, *Zeit. anorg. Chem.*, 1896, **11**, 305. See also Richards, *ibid.*, 1905, **47**, 145.

Strontium Monoxide or Caustic Strontia, SrO.—This substance is obtained by the ignition of the nitrate in the form of a greyish-white porous mass, which becomes crystalline at about 2,500° and melts at about 3,000° (Moissan). When brought into contact with a small quantity of water the monoxide unites with it to form a white powder of *strontium hydroxide*, $Sr(OH)_2$. This body possesses a specific gravity of 3·625, and when strongly heated is reconverted into strontia. The hydroxide is easily soluble in hot water, and the solution, on cooling, deposits transparent tetragonal crystals of the hydrate $Sr(OH)_2,8H_2O$; 100 parts of cold water dissolve 2·0, and of boiling water 41·66 parts of the crystals. Strontia water has a strongly alkaline reaction and possesses caustic properties less marked than the solutions of the alkalis.

Considerable quantities of strontium hydroxide are used in the refining of sugar.

Strontium Dioxide, SrO_2.—Pearly scales of the hydrated dioxide, $SrO_2,8H_2O$, separate out on mixing a solution of the hydroxide with hydrogen dioxide; these lose water on heating, leaving the anhydrous dioxide as a light white powder which does not melt at a red-heat, but gradually loses oxygen (Schöne).

Strontium Hydride, SrH_2, is prepared by heating strontium, or its amalgam, or an alloy containing 55 per cent. of cadmium, in hydrogen, and is a white solid, which forms at a red heat and decomposes when more strongly heated, its dissociation pressure being 100 mm. at 1000°. In its general properties it closely resembles calcium hydride.[1]

Strontium Chloride, $SrCl_2$, is obtained by dissolving strontianite in hydrochloric acid. The hot concentrated solution deposits, on cooling, long hexagonal needles, $SrCl_2,6H_2O$, which are isomorphous with the corresponding hydrate of calcium chloride. They possess a sharp, bitter taste, have a specific gravity of 1·603, and effloresce on exposure to the air. On heating, these crystals yield the anhydrous salt as a white powder, which melts at 873° and when again cooled forms a white semi-transparent glassy mass having a specific gravity of 3·05. According to Mulder 100 parts of water dissolve:—

At	0°	20°	40°	60°	80°	100°	118°·8
$SrCl_2$	44·2	53·9	66·7	83·1	92·4	101·9	116·4.

[1] Guntz, *Compt. rend.*, 1901, **133**, 1209; **134**, 838; Gautier, *Compt. rend.*, 1901, **134**, 100, 1108.

The hexahydrate passes into the dihydrate, $SrCl_2,2H_2O$, at 65·5° in contact with a saturated solution. Chloride of strontium also dissolves in alcohol. The commercial salt frequently contains calcium chloride.

A crystalline compound, $SrCl_2,ICl_3,8H_2O$, has been described.

Strontium Sulphide, SrS, can be obtained crystallised in cubes by heating the sulphate with carbon in the electric furnace,[1] and is also formed by heating the carbonate with sulphur, and the carbonate or oxide in a stream of sulphuretted hydrogen.[2] Like the sulphides of calcium and barium, it is strongly phosphorescent in the presence of small amounts of certain foreign substances, whilst the pure sulphide does not possess this property. The most brilliant green phosphorescence is obtained in the presence of traces of sodium carbonate and chloride and bismuth nitrate, but manganese salts produce a similar phosphorescence.[3]

Strontium Sulphate, $SrSO_4$, is found in large, well-developed rhombic crystals and as a fibrous amorphous mass. It frequently possesses a light blue colour, whence it takes its name celestine (*cœlestis*). When sulphuric acid or a soluble sulphate is added to a solution of a strontium salt, the sulphate is thrown down as a white precipitate possessing a specific gravity of 3·707, and fusing when strongly heated. It is but very slightly soluble in cold, and still less in boiling water. One litre of water at 18° dissolves 0·114 gram (Kohlrausch). Strontium sulphate is much more easily soluble in acids and in solution of common salt, as well as in other salt solutions, but is less soluble in sulphates or dilute sulphuric acid, and is completely decomposed by boiling with a solution of an alkali carbonate. When the salt is dissolved in hot concentrated sulphuric acid, crystals of celestine separate out on cooling, but when it is treated with concentrated sulphuric acid at 100°, and the solution digested with an excess of the salt at a somewhat higher temperature, the compound $H_2SO_4,SrSO_4$ separates out as a granular crystalline powder, which when exposed to moist air changes into small glittering tablets having the composition $H_2SO_4,SrSO_4,H_2O$.

Strontium Nitrate, $Sr(NO_3)_2$, is obtained by dissolving the

[1] Mourlot, *Compt. rend.*, 1898, **127**, 408; Müller, *Centr. Min.*, 1900, 178.

[2] Mourelo, *Compt. rend.*, 1897, **124**, 1024, 1237; **125**, 775.

[3] *Compt. rend.*, 1897, **125**, 1098; 1898, **126**, 420, 904, 1508; **127**, 229, 372; 1899, **128**, 557, 1239. See also Lenard and Klatt, *Ann. Phys. Chem*, 1889, **38**, 90; Waentig, *Zeit. physikal. Chem.*, 1905, **51**, 435.

carbonate in warm dilute nitric acid. When the solution is evaporated down, the anhydrous salt separates out in transparent octahedra or in combinations of the octahedron and the cube. When a dilute solution is cooled down, the hydrate, $Sr(NO_3)_2,4H_2O$, separates out in large, well-developed monoclinic crystals which quickly effloresce on exposure to the air. One hundred parts of water dissolve, according to Mulder:

At	10°	20°	40°	60°	80°	100°	107°·9
$Sr(NO_3)_2$	54·9	70·8	91·3	94·0	97·2	101·1	102·9.

The transition point for the tetrahydrate and the anhydrous salt is 31·3°. Strontium nitrate is insoluble in concentrated nitric acid, and only very slightly soluble in absolute alcohol; it possesses a cooling taste, and has a specific gravity of 2·962 (Schröder). When thrown on to red-hot charcoal it deflagrates, burning with a red flame, and is on this account largely used for pyrotechnic purposes.

The *nitride*,[1] *arsenide*,[2] *phosphide*,[3] and *boride*[4] of strontium closely resemble the corresponding calcium compounds.

Strontium Carbonate, $SrCO_3$, occurs as strontianite in crystals which are isomorphous with those of aragonite. This compound is obtained in the form of a white impalpable powder having a specific gravity of 3·62, when a strontium salt is precipitated by an alkali carbonate. When gently ignited it loses all its carbon dioxide and is converted into strontia. In a current of carbon dioxide, it is converted into oxide at 1155°.[5] One litre of water dissolves 11·0 mgrms. of this salt at 18°.[6] It is less soluble in water containing ammonia, but dissolves considerably in a solution of ammonium chloride and of ammonium nitrate. When boiled with ammonium chloride it is converted into strontium chloride.

Detection and Estimation of Strontium.

271 Strontium salts colour the flame a magnificent crimson. When examined by the spectroscope the spectrum is found to consist of numerous bright lines or bands due to the salts and

[1] Gautier, *Compt. rend.*, 1902, **134**, 1108.

[2] Lebeau, *ibid.*, 1899, **129**, 47. [3] Jaboin, *ibid.*, 1889, **129**, 762.

[4] Moissan, *ibid.*, 1897, **125**, 629.

[5] Brill, *Zeit. anorg. Chem.*, 1905, **45**, 275.

[6] Bineau, *Ann. Chim. Phys.*, 1887, [3], **51**, 290. Compare Kohlrausch and Rose, *Zeit. physikal. Chem.*, 1893, **12**, 241; Hollemann, *Zeit. physikal. Chem.*, 1893, **12**, 125.

oxide of the metal, of which eight are specially characteristic, six in the red, one in the orange, and one in the blue. The orange line, termed Sr α (6045 A.U.), the red, Sr β, and Sr γ, and the blue line, Sr δ (4608 A.U.), are the most intense, and therefore the most valuable for the discrimination of this element.[1] By means of spectrum analysis $\frac{6}{100000}$ mgrm. of strontium chloride can be detected. H. Fox Talbot[2] was the first to describe the spectrum of strontium. He examined the spectrum of the red fire of theatres and distinguished many of the strontium lines, especially the blue line, Sr δ (p. 149). In order to detect strontium the bead, either alone or moistened with hydrochloric acid, is brought into the flame. If strontium be supposed to be present as sulphate the bead is held for a few moments in the reducing portion of the flame, and then moistened with hydrochloric acid in order to convert the strontium sulphide which is formed into strontium chloride. The strontium salts containing non-volatile acids are melted on a platinum wire with a small quantity of sodium carbonate. The fused bead is then reduced to a fine powder and dissolved in a little hot water, and the residue, which contains strontium carbonate, moistened with hydrochloric acid, and the chloride brought on a wire into the non-luminous flame.

Strontium is separated from the alkali metals by precipitation with ammonium carbonate, and is usually estimated quantitatively as the sulphate by precipitating the solution with sulphuric acid in the presence of alcohol and washing the precipitate with a weaker alcohol. In order to separate it from calcium the mixed carbonates are converted into nitrates and these are treated with absolute alcohol or amyl alcohol,[3] which leave the nitrate of strontium undissolved.

Atomic Weight of Strontium.—The atomic weight of strontium was determined by Marignac[4] from the amount of silver required to precipitate a known weight of pure crystallised strontium chloride, and also from the amount of strontium sulphate formed from the chloride; he thus obtained the numbers 86·64 and 86·76 respectively. Richards,[5] from the determination of the amount of silver required to precipitate a known quantity of pure strontium bromide and the

[1] See Riesenfeld and Wohlers, *Ber.*, 1906, **39**, 2628.
[2] *Brewster's Journ. of Science*, 1826, **5**.
[3] Browning, *Amer. J. Sci.*, 1892, **43**, 50.
[4] *Annalen*, 1858, **106**, 165. [5] *Zeit. anorg. Chem.*, 1895, **8**, 253.

quantity of silver bromide formed, obtained as the average of a number of consistent experiments the figure 87·663 (O = 16). A later determination[1] of the ratio of silver to strontium chloride gave the value 87·661.

On the basis of Richards' work, and after revision of the fundamental values,[2] the figure 87·62 was taken as the atomic weight of strontium, In 1910, Thorpe and Francis[3] determined the ratios $2Ag : SrBr_2$, $2AgBr : SrBr_2$, $2Ag : SrCl_2$, $2AgCl : SrCl_2$, $SrBr_2 : SrSO_4$, $SrCl_2 : SrSO_4$, and arrived at a mean value of 87·65. The figure at present (1913) adopted as the atomic weight of strontium is 87·63.

BARIUM. Ba = 137·37

272 Our knowledge of the barium compounds commences with that of the natural sulphate or heavy spar. This substance was first examined in the year 1602, by a Bolognese shoemaker, V. Casciorolus, who noticed that it possessed the remarkable property of becoming phosphorescent when ignited with carbonaceous matter. To this material the discoverer gave the name of *lapis solis*, but it became better known as Bolognian or Bononian phosphorus, from the place in which it was first prepared, whence specimens of the shoe-maker's handiwork found their way into the laboratories of the alchemists of the time. The mineral which yielded this phosphorus, termed Bolognian spar, was first believed to be a peculiar kind of gypsum, and hence it was termed *gypsum spathosum*. In consequence of its high specific gravity, Cronstedt termed it *marmor metallicum*, and Marggraf in 1750, finding that it contained sulphuric acid, ranked it amongst what were then termed the heavy fluor-spars. The nature of this mineral remained for some time obscure, and the learned mineralogist v. Justi wrote in 1760 concerning it as follows: "Our analysis has here reached its limits; we know of no smelting operation by which anything can be got out of this spar. Many profound chemists and skilful assayers have here tried their art in vain." The next step in our knowledge of this subject was made in the

[1] Richards, *Zeit. anorg. Chem.*, 1905, **47**, 145.
[2] *Proc. Chem. Soc.*, 1909, **25**, 7.
[3] *Proc. Roy. Soc.*, A., 1909–10, **83**, 277.

year 1774, when Scheele, who was engaged in his investigation on the black oxide of manganese, examined a specimen of this mineral which he found to contain a new earth, and this when brought in contact with sulphuric acid yielded a salt insoluble in water, which could be brought into a soluble condition by ignition with carbon and an alkali. Gahn afterwards showed that this earth was contained in heavy-spar, and Bergman gave it the name *terra ponderosa*. Guyton de Morveau in 1779 proposed the name barote (from *βαρύς*, heavy), and this name, slightly altered to baryta by Lavoisier, was soon generally adopted. The suggestion that this earth was the oxide of a metal was frequently made, but the fact was not proved until after Davy's discovery of the decomposition of the alkalis.

Barium occurs in nature chiefly as the sulphate or heavy-spar, $BaSO_4$, which is often found together with galena and other metallic ores, though also found not associated with metallic veins. Another source of barium compounds, less widely distributed, is the carbonate or witherite, $BaCO_3$, whilst other minerals containing barium are barytocelestine, $(Ba,Sr,Ca)SO_4$, barytocalcite, $BaCO_3,CaCO_3$, alstonite, $(Ba,Ca)SO_4$, and psilomelane $(Mn,Ba)O,MnO_2$. Many other ores of manganese, especially manganese dioxide, contain small quantities of barium. Barium also occurs as an essential constituent of certain silicates; thus, for instance, brewsterite, $H_4(Sr,Ba)Al_2Si_6O_{18},3H_2O$, harmotome, $H_2(K_2,Ba)Al_2Si_5O_{15},4H_2O$, and hyalophane or baryta-felspar, $(K_2,Ba)_2Al_2Si_8O_{24}$. Many other felspathic rocks also contain traces of barium, and this element occurs likewise in several other minerals and in some soils. It is also found not unfrequently in the ash of trees. Traces are found in mineral waters and in sea-water. Thus, for instance, the old sulphur well at Harrogate contains 6·6 grains of barium chloride per gallon (Hayton Davis),[1] whilst an artesian well at Ilkeston,[2] and the water of the Boston Spa,[3] each contain about 40 parts of barium chloride per 100,000. From sea-water, barium finds its way into sea-plants, and in smaller quantities into the shells and skeletons of sea animals.

Preparation of Metallic Barium.—Davy's first attempts to obtain metallic barium by the electrolysis of baryta were not very successful. Afterwards finding that this did not succeed

[1] Thorpe, *Phil. Mag.*, 1876, [5], **2**, 52.
[2] White, *Analyst*, 1899, **24**, 67.
[3] Richards, *Analyst*, 1901, **26**, 68.

he prepared it from an amalgam, having heard from Berzelius that he and Pontin had succeeded in obtaining it in that way. Davy repeated these experiments and electrolysed baryta, barium chloride, and other barium salts in presence of mercury, heating the amalgam which was thus formed in a tube containing rock oil, when the barium was left behind as a silver-white powder. Bunsen [1] also prepared barium amalgam by the electrolysis of barium chloride in presence of mercury, and attempted to obtain the pure metal by heating this. It has, however, been found that the metal prepared in this way is invariably impure, and cannot be obtained quite pure even by distillation.[2] Small globules of impure barium were obtained by Matthiessen[3] by the electrolysis of fused barium chloride, but the metal was first prepared in a state of purity by Guntz,[4] who employed the same method as for strontium (p. 595). Crude barium, obtained from the amalgam, is converted into the hydride, and this is melted in hydrogen and then heated to 1200° in vacuo. The barium volatilises, and is condensed on a polished steel tube. It can also be prepared by heating baryta with 10 per cent. of its weight of aluminium in vacuo at 1200° and redistilling in vacuo.[5]

Barium is a silver-white metal, of sp. gr. 3·78, melts at about 850°, and boils at about 1150°. It rapidly oxidises, sometimes inflaming spontaneously in the air, and decomposes both water and alcohol. It combines readily with hydrogen and nitrogen when heated in these gases.

COMPOUNDS OF BARIUM.

Barium and Oxygen.

273 *Barium Suboxide*, Ba_2O.—When baryta is heated to 1100° with an atomic proportion of magnesium, half the magnesium distils off, leaving a dark coloured residue, which is considered by Guntz [6] to be a mixture of barium suboxide and magnesia. It decomposes water, yielding an amount of hydrogen

[1] *Pogg. Ann.*, 1854, **91**, 619.
[2] Guntz, *Ann. Chim. Phys.*, 1905, [8], **4**, 5; Stansfield, *Mem. Manch. Phil. Soc.*, 1901, **46**, No. 4.
[3] *Annalen*, 1855, **93**, 277. [4] *Compt. rend.*, 1905, **141**, 1240.
[5] Guntz, *Compt. rend.*, 1906, **143**, 339.
[6] *Compt. rend.*, 1906, **143**, 339.

equivalent to half the barium in the original baryta, and absorbs both nitrogen and hydrogen. A similar dark-coloured mass is obtained by heating barium with baryta.

Barium Monoxide or Baryta, BaO, is formed when the metal burns in the air, but is usually obtained by heating the nitrate in a iron crucible, until no further evolution of red fumes is observed. The mass fuses and is apt to froth over unless care be taken. Mohr has proposed to mix the nitrate with its own weight of sulphate of barium; this prevents the frothing, and for many purposes the presence of insoluble barium sulphate does not matter. If only a small quantity of baryta is required it it best obtained by igniting the iodate, which gives off its iodine and five-sixths of its oxygen without fusing or frothing:

$$2Ba(IO_3)_2 = 2BaO + 2I_2 + 5O_2.$$

It is also prepared by heating barium carbonate to a white heat, the reaction proceeding more readily if this be mixed with one-tenth of its weight of lamp-black or wood-charcoal, carbon monoxide being then evolved:

$$BaCO_3 + C = BaO + 2CO.$$

The material thus obtained sometimes contains a small amount of barium cyanide. Baryta is thus obtained as a greyish-white porous mass, which has a specific gravity of 4·73 (Karsten), 5·46 (Filhol), and melts at about 2,000°, crystallising on cooling in cubes, which have a specific gravity of 5·72. It combines with water with great evolution of heat forming the hydroxide, becoming incandescent if only sprinkled with water. It also unites with oxygen at a red-heat, the oxygen being evolved on further heating, and it has therefore been used for the manufacture of oxygen (Vol. I., p. 246).

Barium Hydroxide, $Ba(OH)_2$, is formed as a white powder by the reaction just described. The hydroxide melts at a low red-heat, forming an oily liquid, which on cooling solidifies to a crystalline mass, and this does not give off water even when more strongly heated. It is prepared on the large scale from barium sulphide, which is heated in earthenware retorts, into which a current of moist carbon dioxide is passed. Superheated steam is then passed over the carbonate, when the following decomposition takes place:

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

It may also be prepared on the large scale by the electrolysis of a solution of barium hydrosulphide.[1] It has a specific gravity of 4·495 (Filhol), and when brought into contact with water forms a crystalline hydrate, $Ba(OH)_2,8H_2O$. This hydrate is soluble, and when a saturated solution is cooled it separates out in tetragonal prisms which are isomorphous with strontium hydroxide. On exposure to air these crystals fall to a white powder with loss of seven molecules of water, forming the monohydrate. They melt in their water of crystallisation at 77·9° (Richards and Churchill),[2] 78° under 732 mm. pressure (Bauer);[3] this solution boils at 103°, and at 109° deposits rhombic crystals of the hydrate with $3H_2O$, which lose $2H_2O$ over sulphuric acid (Bauer). A hydrate with $16H_2O$ is also known. One hundred parts of water dissolve:

At	0°	20°	40°	60°	80°
$Ba(OH)_2$	1·65	3·9	8·3	21·0	101·5 parts.

A solution of the hydroxide is termed *baryta water*, and is largely used in the processes of chemical analysis. It has a more strongly alkaline reaction than lime water, and rapidly absorbs carbon dioxide. It is employed, as has been stated in Vol. I., p. 602, for the estimation of the carbon dioxide contained in the atmosphere, for which purpose it must be free from hydroxides of the alkali metals.

Barium Dioxide, BaO_2.—When heated to redness in a current of dry oxygen, pure baryta absorbs the gas with rapidity, forming the dioxide (Gay-Lussac and Thénard); it is also formed by heating baryta and potassium chlorate to low redness (Liebig and Wöhler). The hydroxide when heated to redness in a current of air also yields the dioxide (Boussingault). In Brin's process for the manufacture of oxygen it is obtained as an intermediate product by heating pieces of baryta of the size of walnuts to 700° in steel retorts, and passing air through these under an additional pressure of 15 lb. per square inch. The product obtained by any of these methods is a greyish porous mass, and usually contains silica, lime, and also ferric oxide derived from the vessels in which it is prepared. To obtain it in the pure state it is treated in the manner already described under hydrogen peroxide (Vol. I., p. 338); then

[1] Brocket and Ransom, *Compt. rend.*, 1903, **136**, 1258.
[2] *Zeit. physikal. Chem.*, 1898, **28**, 313.
[3] *Zeit. anorg. Chem.*, 1905, **47**, 401.

when dried at 130° it forms an impalpable white powder, which can hardly be distinguished from magnesia. It can readily be prepared on the small scale by adding hydrogen peroxide to a solution of baryta water. It fuses at a bright red-heat with loss of one atom of oxygen, and combines with water to form the hydrate $BaO_2,8H_2O$, crystallising in microscopic hexagonal plates, which are only very slightly soluble in water. It also appears to form several compounds with different proportions of hydrogen peroxide.[1]

Barium and Hydrogen.

274 *Barium Hydride,* BaH_2, is formed when barium amalgam is heated in an iron boat to 1400° in a current of hydrogen. It forms a grey, crystalline mass of sp. gr. 4·21, melts at about 1200° and is decomposed by water.[2] When heated in nitrogen, hydrogen is evolved and the nitride produced.

Barium and the Halogens.

275 *Barium Chloride,* $BaCl_2$, is most readily obtained by dissolving witherite in dilute hydrochloric acid. As, however, this mineral contains calcium, lead, iron, and manganese compounds, an excess of barium carbonate is added to the solution and the liquid allowed to remain in contact with it for some time. In this way the oxides of the above metals are precipitated, while the rapidity of the precipitation can be increased by the addition of a small quantity of baryta water. The clear solution is then neutralised with hydrochloric acid and evaporated to the point of crystallisation. On the large scale the salt is easily prepared from heavy-spar. For this purpose 100 parts of the finely powdered mineral are mixed with from 35 to 50 parts of carbon, from 15 to 25 parts of limestone, and from 40 to 60 parts of calcium chloride. This mixture is heated in a reverberatory furnace, and the mass lixiviated with water, when insoluble calcium sulphide remains behind and the barium dissolves as chloride.

Barium chloride crystallises with $2H_2O$ in colourless rhombic

[1] de Forcrand, *Compt. rend.*, 1900, **130**, 716, 778, 834.

[2] Guntz, *Compt. rend.*, 1901, **132**, 963; Gautier, *ibid.*, 1902, **134**, 1108.

tablets (Fig. 155), which do not undergo any alteration in the air and have a specific gravity of 3·097. 100 parts of water dissolve :

At	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°	104·1°
$BaCl_2$	33·3	35·7	38·2	40·8	43·6	46·4	49·4	52·4	55·6	58·8	60·3.

Barium chloride is less soluble in dilute hydrochloric acid than it is in water. It is almost insoluble in the concentrated acid, and also but slightly soluble in strong nitric acid, and for this reason these acids precipitate concentrated solutions of a barium salt. Absolute alcohol does not dissolve barium chloride, and addition of alcohol to its aqueous solutions precipitates the salt.

Crystallised barium chloride loses its water at a temperature of 113°, forming the anhydrous salt as a white powder of sp. gr. 3·856, which melts at 960° (Ruff and Plato) and on cooling solidifies to a translucent mass. On exposure to the air the chloride in a state of fusion parts with a small quantity of

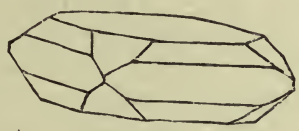


Fig. 155.

chlorine, baryta being formed. Hence the fused salt usually has an alkaline reaction. When heated in a current of steam it emits hydrochloric acid at a temperature below its fusing point. Barium chloride has an unpleasant bitter taste and acts as a powerful poison. Its chief use is for the preparation of the artificial sulphate or *permanent white*. It has also been successfully employed for the prevention of incrustation in steam boilers when permanently hard waters are used. All the gypsum contained in solution is decomposed by barium chloride, whilst any calcium carbonate present in solution may be subsequently precipitated by milk of lime. The water thus softened forms no incrustation.

Barium Fluoride melts at 1280°, the *bromide* at 880°, and the *iodide* at 740° (Ruff and Plato).

Subhalogen Salts of Barium.—Like calcium and strontium, barium appears to form a series of halogen salts in which it is monovalent. The subchloride, BaCl, is formed at the cathode by the action of barium on the chloride during the electrolysis of the latter, and decomposes water readily. A series of

crystalline double salts with the halogen salts of sodium can be obtained by heating the barium halogen salts with metallic sodium. The compound BaCl,NaCl, prepared in this way decomposes water, loses metallic sodium at 700° in vacuo, and when treated with mercury yields barium amalgam.[1]

Barium Chlorate, $Ba(ClO_3)_2$, is obtained by adding barium chloride to a solution of sodium chlorate, double decomposition taking place:

$$2NaClO_3 + BaCl_2 = Ba(ClO_3)_2 + 2NaCl.$$

The solution on concentration deposits sodium chloride, which is fished out; the remaining solution is then evaporated and the barium chlorate purified by recrystallisation. It crystallises with one molecule of water in monoclinic prisms which readily dissolve in water and alcohol, the latter solution burning with a characteristic green flame. If a drop of sulphuric acid be brought on to a mixture of the salt and powdered sugar it takes fire and burns with a bright green flame, and if the chlorate in a state of fusion and strongly heated be plunged into an atmosphere of coal-gas, combustion also takes place, the oxygen of the chlorate combining with the carbon and hydrogen of the coal-gas. It is largely used for pyrotechnic purposes.

Barium Iodate, $Ba(IO_3)_2$.—This salt is employed for the preparation of iodic acid. It is obtained as a white granular precipitate by adding potassium iodate to barium chloride (Vol. I., p. 367). Barium iodate dissolves in about 4,500 parts of cold and 500 parts of boiling water. It also dissolves in hot nitric acid, from which solution it crystallises, on cooling, with one molecule of water in bright glittering monoclinic prisms; these are isomorphous with those of the chlorate and are decomposed by hydrochloric acid with evolution of iodine.

Barium and Sulphur.

276 *Barium Monosulphide*, BaS, is obtained when sulphuretted hydrogen is passed over heated baryta as long as water is formed. On the large scale it is prepared by roasting 20 parts of slack or pitch with 100 parts of heavy spar. In order to assist the

[1] Guntz, *Compt. rend.*, 1903, **136**, 749; Haber and Tolloczko, *Zeit. anorg. Chem.*, 1904, **41**, 407.

evolution of the carbon dioxide sawdust may be added to the mixture. It can be obtained crystalline[1] by fusing the amorphous salt in the electric furnace, and then has the sp. gr. 4·3. Barium sulphide decomposes in contact with water into barium hydroxide and barium hydrosulphide:

$$2BaS + 2H_2O = Ba(SH)_2 + Ba(OH)_2.$$

When a solution of 5 parts of the sulphide is boiled with 1 part of sulphur, and the solution is allowed to evaporate in a vacuum, colourless, transparent six-sided tables of $BaS,6H_2O$, or possibly $BaSH(OH),5H_2O$, are deposited. When these crystals are treated with a small quantity of water, barium hydrosulphide dissolves and barium hydroxide remains behind.

Barium Hydrosulphide, $Ba(SH)_2$, is prepared by saturating water with barium hydroxide in an atmosphere of hydrogen at 100°, and passing sulphuretted hydrogen free from oxygen through the solution heated to 60—70° for several days.[2] It crystallises with $4H_2O$ in aggregates of colourless, spear-shaped needles, which dissolve in water and lose sulphuretted hydrogen readily when heated, so long as water is also driven off, the sulphur then remaining only being given off at a red heat.

Barium Tetrasulphide, BaS_4, is obtained by boiling aqueous solutions of the sulphide or hydrosulphide with sulphur, and forms red crystals, containing according to Schöne $1H_2O$, and according to Veley, $2H_2O$. It dissolves in water, forming a deep red solution. A *barium trisulphide* and *pentasulphide* have also been described, but their existence is doubtful.

Bononian Phosphorus.—The Bononian phosphorus which has been already mentioned (p. 601) is best prepared by heating 5 parts of precipitated barium sulphate together with 1 part of powdered charcoal over an ordinary gas flame for 30 minutes, and then igniting it more strongly over a gas blowpipe for ten minutes. Whilst hot the mass must be filled into glass tubes and the tubes sealed. After exposure to sunlight or to the light of burning magnesium wire this mass phosphoresces in the dark with a bright orange-coloured light. The pure sulphide, like pure sulphide of calcium and of strontium, does not exhibit phosphorescence, but does so in the presence of small quantities of many metallic salts.[3]

[1] Mourlot, *Compt. rend.*, 1898, **126**, 643.
[2] Veley, *Journ. Chem. Soc.*, 1886, **49**, 369.
[3] Lenard and Klatt, *Ann. Phys.*, 1904, (4), **15**, 225, 425.

Barium Sulphate, $BaSO_4$, is by far the commonest and most widely distributed of the barium compounds, and occurs as heavy-spar, which crystallises in the rhombic system, Figs. 156—158. If anhydrous baryta be brought into contact with fuming sulphuric acid, or even with sulphuric acid which contains a small quantity of water, combination takes place with such rapidity that the mass becomes incandescent. On the other hand, pure sulphuric acid which has the exact composition, H_2SO_4, does not act upon baryta, but if the mixture be touched in one place with a hot iron or with a moistened glass-rod, combination begins and is at once propagated throughout the mass (Kuhlman). Sulphuric acid and its salts precipitate the sulphate from a solution of a soluble barium salt in the form of a crystalline powder. The pure mineral heavy-spar has a specific

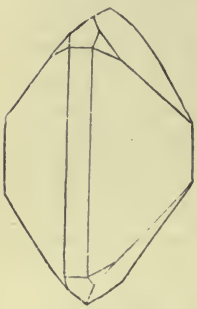


Fig. 156.

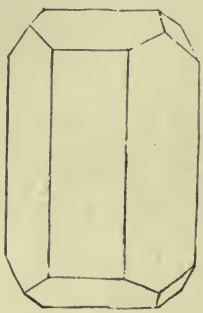


Fig. 157.

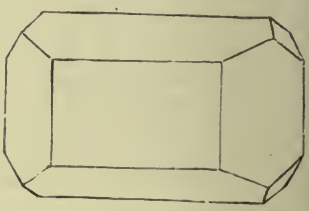


Fig. 158.

gravity of 4·486 (H. Rose), the precipitated salt at 4° having a specific gravity of 4·53 (Schröder). This salt is almost insoluble in water, 1 litre dissolving[1] only 0·0024 gram at 18·3°. The solubility is greatly influenced by the size of the particles of the solid salt.[2] It is somewhat more soluble in dilute acids and in the presence of many salts, *e.g.*, sodium thiosulphate. Barium sulphate is precipitated in a remarkable gelatinous form when dilute sulphuric acid is added to a solution of baryta in methyl alcohol, which when dried and heated forms hard masses resembling porcelain. A number of other salts of the alkaline earth metals can be obtained in a similar form.[3] If a salt of barium be heated with concentrated sulphuric acid, the sulphate dissolves to a certain extent and separates out on cooling in

[1] Küster, *Zeit. anorg. Chem.*, 1896, **12**, 261.
[2] Hulett, *Zeit. physikal. Chem.*, 1901, **37**, 398.
[3] Neuberg and Neimann, *Biochem. Zeit.*, 1906, **1**, 166.

crystals having the composition $H_2SO_4,BaSO_4$; if the acid solution be exposed to moist air bright silky needles are formed having the composition $H_2SO_4,BaSO_4,2H_2O$.

The crude heavy-spar is prepared for use as a paint, either alone or along with white lead, by being finely ground, treated with sulphuric acid to remove salts of iron, washed and dried. Artificial barium sulphate is also manufactured on a large scale and is known as *permanent white*, or *blanc fixé*. This preparation is largely used as a pigment and is much to be preferred for this purpose to the finely ground mineral, inasmuch as the latter, with its denser structure, is transparent and has but little "body" or covering power. In order to prevent the formation of finely divided crystals a solution of barium chloride having a specific gravity of 1·19 is precipitated in the cold with dilute sulphuric acid having a specific gravity of 1·245. The precipitate is washed with cold water and sent to market in the moist state. In addition to its value as a paint, blanc fixé is largely used for giving weight to cards and paper.

Barium Disulphate, BaS_2O_7.—If powdered barium sulphate is intimately mixed with fuming sulphuric acid it dissolves, forming a syrup, which on heating to 150° deposits the disulphate in glistening granular crystals; these do not melt on heating but decompose at a dull-red heat.

Barium Dithionate, $BaS_2O_6,2H_2O$.—This salt is prepared by decomposing the corresponding manganese salt with barium sulphide. On allowing the solution to evaporate in a warm place glittering rhombic crystals of the salt are deposited. It dissolves at 18° in 4·04, and at 100° in 1·1, parts of water. On heating it is converted without change of form into barium sulphate.

Barium Persulphate, BaS_2O_8, is obtained by the action of barium hydroxide on ammonium persulphate, and crystallises in monoclinic prisms which are readily soluble in water, but gradually decompose on keeping, with formation of barium sulphate.

Barium and Nitrogen.

277 *Barium Nitride*, Ba_3N_2, is obtained by passing nitrogen over barium or barium amalgam heated to redness, but is best prepared by heating barium amide at 430° in a vacuum.[1] It

[1] Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], **29**, 578.

forms a voluminous yellow powder, which volatilises slightly at 1,000° without melting. It is decomposed by water with formation of ammonia and barium hydroxide, and yields barium cyanide when heated in a current of carbonic oxide.[1]

Barium Azoimide, $Ba(N_3)_2$, obtained from ammonium nitride solution by boiling with baryta, forms hard, lustrous crystals which explode at 217°.

Barium Amide, $Ba(NH_2)_2$.—When ammonia is passed over cooled metallic barium a red mass and then a blue liquid is formed, which is regarded by Mentrel[2] as a solution of *barium ammonium*, $Ba,6NH_3$ in ammonia, but is more probably[3] a solution of metallic barium in liquid ammonia (see p. 379). At 200° ammonia is decomposed by barium with formation of the amide,[4] which is a greyish-white mass and melts at 280°.

Barium Nitrite, $Ba(NO_2)_2$, can be readily prepared by bringing a mixture of 360 grams of sodium nitrite and 610 grams of barium chloride into a boiling solution of 360 grams of sodium nitrite, filtering from the sodium chloride which is precipitated, cooling and recrystallising. It crystallises with $1H_2O$ in prisms, and serves as a convenient source for the preparation of the nitrites of other metals.[5]

Barium Nitrate, $Ba(NO_3)_2$.—This salt is prepared on the large scale either by decomposing the carbonate or sulphide by dilute nitric acid, or by mixing hot saturated solutions of sodium nitrate and barium chloride. On cooling, the larger portion of the barium nitrate crystallises out, and the remaining portion is obtained by evaporating the mother liquors. Barium nitrate crystallises in combinations of the cube and octahedron, and in other more complicated forms of the regular system (Lewis). Its specific gravity is 3·2; it possesses an acrid taste and melts at a temperature of 593° (Carnelley). 100 parts of water dissolve:

At	0°	10°	20°	50°	80°	100°	102°
$Ba(NO_3)_2$	5·0	7·0	9·2	17·1	27·0	32·2	34·8.

The salt is insoluble in concentrated nitric acid and in absolute alcohol, and dissolves only sparingly in these liquids diluted with

[1] Maquenne, *Compt. rend.*, 1892, **114**, 25, 220.
[2] *Compt. rend.*, 1902, **135**, 740.
[3] Ruff and Geisel, *Ber.*, 1906, **39**, 828.
[4] Guntz and Mentrel, *Bull. Soc. chim.*, 1903, [3], **29**, 578.
[5] Witt and Ludwig, *Ber.*, 1903, **36**, 4384. See also Arndt, *Zeit. anorg. Chem.*, 1901, **27**, 341.

water. Barium nitrate is largely used for pyrotechnic purposes, especially for the preparation of green fire, and for the manufacture of an explosive powder known as *saxifragin*, which consists of a mixture of 76 parts of nitrate of barium, 22 parts of carbon, and 2 parts of nitre.

Barium and Carbon.

278 *Barium Carbide*, BaC_2.—This substance is obtained by heating baryta with charcoal in an electric furnace, and closely resembles the corresponding calcium compound. Its behaviour on heating in nitrogen is, however, different from that of calcium, which forms calcium cyanamide. Barium carbide forms the cyanide:[1]

$$BaC_2 + N_2 = Ba(CN)_2.$$

Barium Carbonate, $BaCO_3$.—Barium carbonate occurs in nature as witherite. This mineral was discovered at Leadhills in Scotland by Withering in the year 1783. It crystallises in rhombic prisms and pyramids, is isomorphous with aragonite, and is chiefly found in England, one of its most celebrated localities being Fallowfield in Northumberland. It occurs also in Silesia, Hungary, Styria, Russia, Chili, and other places. Alstonite, $(Ba,Ca)CO_3$, is isomorphous with witherite, and contains the two metals in varying proportions. Baryto-calcite, on the other hand, has the formula $BaCO_3,CaCO_3$, and crystallises in the monoclinic system.

Artificial barium carbonate is a dense white powder of sp. gr. 4·275, obtained when a solution of chloride of barium is poured into an excess of a hot solution of ammonium carbonate. Barium carbonate appears to undergo a polymorphic change[2] at 811°, and does not melt below 1,350° when heated in an atmosphere of carbon dioxide.[3] When heated in the air a basic carbonate, $BaO,BaCO_3$, appears to be formed, which melts below 980°. The dissociation pressure is 2·7 mm. of carbon dioxide at 1,000° and 381 mm. at 1,300°.

One litre of water dissolves only about 0·02 gram of barium carbonate at 18°, but it is more readily soluble in water containing carbonic acid. The artificial salt is employed in

[1] Erlwein, *Zeit. Elektrochem.*, 1903, **9**, 842.
[2] Boeke, *Zeit. anorg. Chem.*, 1906, **50**, 1244.
[3] Finkelstein, *Ber.*, 1906, **39**, 1585.

chemical analysis, and powdered witherite in the preparation of other barium salts and as a rat bane.

Barium Percarbonate, $BaCO_4$,[1] is prepared by passing carbon dioxide into cold water in which barium peroxide is suspended. It is insoluble in water, and in the dried condition slowly gives off oxygen, being converted into the carbonate.

Silicates of Barium.—It has been already stated that many of these salts occur as crystalline minerals. Barium silicate is also a constituent of baryta-glass, a flint glass in which the lead has been replaced by barium (p. 573).

Detection and Estimation of Barium.

279 The non-luminous gas-flame is coloured a yellowish-green tint when any volatile barium compound is brought into it. The barium compounds yield the most complicated of the spectra of the alkalis and alkaline earths. The spectrum is, however, at once distinguished by the green lines Baα and Baβ, which are by far the most distinct, appearing the first and continuing during the whole of the experiment. Baγ is not nearly so distinct, but is still a well-marked and characteristic line. As the spectrum of the barium compounds is more extended than the spectra of the compounds of the other metals, the reaction is not observed with so great a degree of delicacy, but it appears from Bunsen's experiments that about $\frac{1}{1000}$ of a milligram of barium salt may be detected with the greatest certainty. The chloride, bromide, iodide, and fluoride of barium, as well as the hydroxide, the sulphate, and carbonate, show the reaction best. It may be obtained by simply heating any of these salts in the flame. Silicates containing barium which are decomposed by hydrochloric acid give the reaction, if a drop of hydrochloric acid is added to them before they are brought into the flame. Baryta-harmotome, treated in this way, gives the lines Caα and Caβ, together with the bands Baα and Baβ. Compounds of barium with fixed acids, giving no reaction either when alone or after addition of hydrochloric acid, should be fused with carbonate of sodium, as described under strontium, and the carbonate of barium thus obtained examined. If barium and strontium occur in small quantities together with large amounts of calcium, the carbonates obtained by fusion are dissolved in nitric acid and the dry salt extracted with alcohol;

[1] D. R. P., 178019.

the residue contains only barium and strontium, both of which can almost always be detected. To test for very small traces of strontium or barium, the residual nitrates are converted into chlorides by ignition with sal-ammoniac, and the chloride of strontium is extracted by alcohol. Unless one or more of the bodies to be detected is present in very small quantities, the methods of separation just described are quite unnecessary. The detection of these three metals by the spectroscope is much facilitated by the use of a special burner in which a spray of the solution of the salts to be examined is brought into the flame.[1]

Soluble barium salts are distinguished from those of strontium and calcium, inasmuch as they are *immediately* precipitated by a solution of calcium sulphate. The qualitative separation of barium from strontium and calcium is usually effected by the addition of potassium chromate to a solution of the mixed salts containing acetic acid, barium chromate being precipitated. Barium and strontium may be separated by treating the mixed chlorides with absolute alcohol, or preferably by the action of amyl alcohol on the mixed bromides,[2] the barium salt being almost insoluble in both solvents. For quantitative estimation barium is almost always weighed as the sulphate, but in some special cases as the carbonate.

Atomic Weight of Barium.—The atomic weight of barium was determined by Marignac from the exact quantity of silver required to precipitate a known weight of crystallised barium chloride, and also from the weight of barium sulphate obtained from the same salt, the number obtained being 136·15. Richards[3] subsequently redetermined the atomic weight by ascertaining the equivalent of both barium chloride and bromide to silver and silver chloride or bromide, and the results, which agree very closely, give the average number Ba 137·37, which is now (1913) adopted.

[1] Riesenfeld and Wohlers, *Ber.*, 1906, **39**, 2628.
[2] Browning, *Amer. J. Sci.*, 1893, **44**, 459.
[3] *Zeit. anorg. Chem.*, 1892, **3**, 441; 1893, **6**, 89.

THE MAGNESIUM GROUP.

280 The elements of this sub-group differ from the metals of the alkaline earths more especially in the properties of the metals themselves, which are much more readily obtained in the free state and only undergo at most a slight superficial oxidation in the air at the ordinary temperature. At higher temperatures they combine with oxygen, forming the oxide corresponding to the divalent series of salts, and magnesium and zinc slowly decompose water at the boiling point. They are colourless and ductile metals, the melting and boiling points of which fall with increasing atomic weight, mercury being a liquid at the ordinary temperature, whilst it solidifies at a low temperature to a malleable solid. Most of the salts closely resemble the corresponding salts of the alkaline earth metals, except that they exhibit a greater tendency to form basic salts, and that the sulphates are readily soluble in water, and yield crystalline double salts. Mercuric sulphate forms an exception, as it is converted by water into an insoluble basic salt and a soluble acid salt, and mercury also differs from the other metals inasmuch as it forms a series of stable salts in which each atom of the metal replaces only one atom of hydrogen, in addition to the series common to all the members of the group, in which the metal is divalent. Some of the magnesium, zinc, and cadmium compounds combine with ammonia forming derivatives analogous to the ammoniacal copper compounds, mercury, in particular, yielding a large series of such derivatives.

GLUCINUM OR BERYLLIUM. Gl = 9·1.

281 Vauquelin in 1798 was the first to detect the existence of the oxide of this metal in beryl, this mineral having formerly been regarded as a compound of silica with lime or alumina.

The earth contained in beryl was shown by Vauquelin to be a distinct body, differing from both lime and alumina, inasmuch as it formed a soluble sulphate which was incapable of uniting with potassium sulphate to form an alum. Haüy had previously observed that emerald was mineralogically identical with beryl, and on examining the former mineral Vauquelin found that it likewise contained the new earth. He did not give any special name to this new earth, but the editors of the *Annales de Chimie* gave it the name of glucina from γλυκύς sweet, because its salts possessed a peculiar sweet taste. As, however, there are other salts which possess the same property, the name beryllia, derived from the mineral, was given to it by the German chemists. The metal has likewise received two names, glucinum and beryllium, the former of which is to be preferred on historical grounds and is adopted here, although the latter is still employed by chemists in Germany.

Glucinum occurs in many minerals, especially in beryl, $Gl_3Al_2Si_6O_{18} = 3GlO,Al_2O_3,6SiO_2$, crystallising in hexagonal prisms, Figs. 159, 160, and 161 (Class 27, p. 201), which

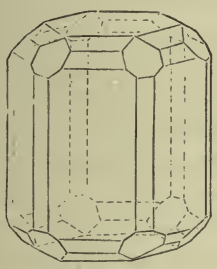


Fig. 159.

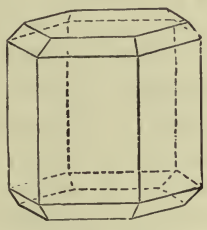


Fig. 160.

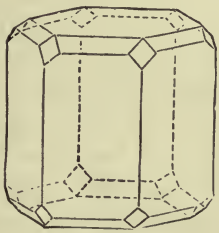


Fig. 161.

usually have a green colour, colourless beryl being seldom met with. The transparent green-coloured varieties of beryl are known as emerald, those possessing a bluish-green tint being termed aquamarine; the green colour of emerald is probably due to traces of chromium. Beryl occurs also of a blue, yellow, grey, and rose-red tint. When the mineral is transparent it is termed precious beryl: when translucent or opaque it is known as common beryl. Glucinum also occurs in leucophane, $NaCaGlF(SiO_3)_2$; in phenacite, Gl_2SiO_4; euclase, $H_2O,2GlO,Al_2O_3,2SiO_2$; and chrysoberyl, GlO,Al_2O_3, as well as in other minerals.

Metallic Glucinum was first obtained by Wöhler in the year 1828 by fusing the chloride with potassium. Prepared in this

way glucinum is a dark-grey powder, which under the burnisher assumes a bright metallic lustre.[1]

Debray first obtained the metal in a coherent state by placing in a glass tube two or more boats made of a mixture of clay and lime, the first containing glucinum chloride and the others metallic sodium. The air having been replaced by dry hydrogen, the boats were heated, by which means the glucinum chloride was vaporised and then reduced by the melted sodium. Later, Nilson and Pettersson[2] prepared it by heating potassium glucinum fluoride with the calculated quantity of sodium in a steel crucible. Glucinum can also be prepared by the electrolysis of a fused mixture of the chloride with sodium chloride and ammonium chloride,[3] or of the fused double fluorides, $GlF_2,2NaF$, or GlF_2,NaF, the pure halogen salts offering too great a resistance to the current.[4] The metal has a specific gravity of 1·93, and a specific heat of 0·4246 (Nilson and Pettersson), giving an atomic heat of 3·9 (see p. 19). It is a hard metal, possesses a bright silver-white colour,[5] melts at a lower temperature than silver, and when heated before the blowpipe becomes covered with a film of oxide which prevents further oxidation. In the finely powdered state, on the other hand, it takes fire when heated in the air and burns with great brilliancy. The powdered metal dissolves in dilute acids; the compact form is readily soluble in dilute hydrochloric acid, but dilute sulphuric acid dissolves it only when warm, whilst concentrated nitric acid does not attack it in the cold, and on heating does so only slowly. The metal does not decompose water even at a red heat (Debray). Ammonia does not act either on the powder or on the compact metal, but both forms dissolve readily in caustic potash with evolution of hydrogen.

[1] *Ann. Chim. Phys.*, 1855 (3), **44**, 5.

[2] *Ann. Phys. Chem.*, 1878, **4**, 554.

[3] Borchers, *Journ. Chem. Soc.*, 1896, **70**, ii., 521.

[4] Lebeau, *Compt. rend.*, 1898, **126**, 744. Compare Warren, *Chem. News*, 1895, **72**, 310.

[5] Compare on this point Kahlbaum and Sturm, *Zeit. anorg. Chem.*, 1905, **46**, 237.

GLUCINUM COMPOUNDS.

Glucinum and Oxygen.

282 *Glucinum Oxide, Glucina,* or *Beryllia,* BeO.—To obtain this earth from beryl the latter is fused with twice its weight of potassium carbonate and the melt treated with sulphuric acid; the excess of acid is evaporated off, water added, the silica removed by filtration and the solution concentrated. Almost the whole of the aluminium separates out on cooling as alum, and the mother liquor then contains chiefly the sulphates of glucinum and iron with small quantities of alum. To separate the glucinum advantage is taken of the solubility of glucinum hydroxide and carbonate in an excess of ammonium carbonate solution, the iron and alumina being left for the most part undissolved. In carrying out the separation the mother-liquor is poured into a concentrated solution of ammonium carbonate, the liquid allowed to stand for several days, and the precipitated iron and aluminium salts filtered off. The filtrate on boiling deposits a basic glucinum carbonate together with a little ferric hydroxide.[1]

To prepare pure glucina from this precipitate, it is redissolved in ammonium carbonate solution, and a strong current of steam blown through the liquid, which precipitates the glucina; this process is repeated several times, and the final precipitate is dissolved in hydrochloric acid, precipitated with ammonia, washed, and dried.[2] According to Krüss[3] it then still contains a small quantity of impurity, which is removed by redissolving in ammonium carbonate solution, adding a little ammonium sulphide, and allowing it to stand for several days. A slight black precipitate is formed, and the filtered solution yields pure glucina.

According to Gibson the best method of preparing glucina from beryl is as follows:—Coarsely powdered beryl is heated with 6 parts of ammonium hydrogen fluoride for 10—12 hours at a heat not exceeding dull redness. The aluminium is thus almost completely converted into insoluble aluminium fluoride, and the residue on treatment with water yields a solution con-

[1] Joy, *Amer. J. Sci.*, 1863 (2), **6**, 83.
[2] Humpidge, *Proc. Roy. Soc.*, 1886, **39**, 1.
[3] *Ber.*, 1890, **23**, 727.

taining chiefly glucinum and iron fluorides. This is evaporated to dryness, and heated with strong sulphuric acid until the ferric sulphate formed commences to decompose, fluorine and silicon being thus completely removed. The solution obtained on adding water is boiled with nitric acid to oxidise the iron to the ferric state, and the filtered liquid poured into an excess of concentrated ammonium carbonate solution. The bulk of the iron separates on addition of an equal volume of hot water, and the filtrate is then mixed with an excess of mercuric chloride and precipitated with ammonium sulphide, the whole of the iron coming down together with the mercuric sulphide, whereas it is only partially precipitated if no mercuric chloride be first added. The filtered solution is boiled to precipitate the basic glucinum carbonate, which on ignition yields pure glucina, any traces of ammonium and mercury salts being volatilised with the carbon dioxide.[1]

To prepare glucina from leucophane, the latter, after separation from admixed tourmaline, is heated with sulphuric acid to remove fluorine, the excess of acid boiled off, the residue boiled with water, and the filtered extract added to an excess of ammonium carbonate solution. After ten days the solution is filtered, the filtrate boiled, and the precipitated crude basic glucinum carbonate treated in the manner already described.[2]

Glucina is a white amorphous powder having a specific gravity of 3·016, which when heated to the highest temperature of a wind furnace assumes the form of microscopic prisms resembling corundum (Rose). It may be easily obtained in this form by the ignition of a mixture of glucinum and potassium sulphates (Debray), and when fused in the electric arc forms a crystalline mass,[3] harder than ruby, which has the specific gravity 3·025. It is insoluble in water, and only dissolves in dilute acids when it has not been strongly ignited. Concentrated boiling sulphuric acid dissolves it easily, and if it be fused with an alkali, and the cold mass treated with water, the glucina goes into solution.

Glucinum Hydroxide, $Gl(OH)_2$.—This is thrown down as a gelatinous precipitate when a glucinum salt is precipitated with ammonia. This precipitate is soluble in acids, caustic alkalis,

[1] *Journ. Chem. Soc.*, 1893, **63**, 909. Compare Lebeau, *Compt. rend.*, 1895, **121**, 641; Pollok, *Journ. Chem. Soc.*, 1904, **85**, 603.

[2] Krüss and Moraht, *Ber.*, 1890, **23**, 727.

[3] Lebeau, *Compt. rend.*, 1896, **123**, 818.

and alkali carbonates, but when heated with water or dilute ammonia, or when preserved dry, it gradually becomes much less soluble.[1] On drying it forms a voluminous white powder which is converted into the oxide by ignition.

Salts of Glucinum.

283 *Glucinum Chloride*, $GlCl_2$, is obtained in the form of snow-white needle-shaped crystals when a mixture of the oxide and sugar charcoal is ignited in a current of dry chlorine or hydrochloric acid gas. It melts at 440° (Lebeau) and boils at about 520° (Nilson and Pettersson), and the specific gravity of its vapour[2] is 2·72, corresponding to the formula $GlCl_2$. In moist air it fumes similarly to phosphorus pentachloride. It is deliquescent, and dissolves in water with evolution of heat, the solution having an acid reaction, owing to hydrolysis. When the aqueous solution is allowed to evaporate over sulphuric acid, colourless crystals of the hydrated chloride, $GlCl_2,4H_2O$, separate out. A basic chloride is obtained by evaporating the solution to dryness. Glucinum chloride forms double salts with iodine trichloride,[3] platinum chloride, tin chloride, and mercuric chloride. Several basic chlorides have also been described; they are, however, not well defined.

The *iodide*, GlI_2, melts at about 510°, and its vapour burns in the air when strongly heated. The *bromide*, $GlBr_2$, sublimes without melting at 450°. The *fluoride*, GlF_2, melts at about 800°, and is converted by oxygen into the oxyfluoride.[4]

Sulphates of Glucinum.—The normal salt, $GlSO_4,4H_2O$, crystallises from a hot saturated solution in tetragonal pyramids which dissolve at the ordinary temperature in their own weight of water, possess a sweet taste, and effloresce on exposure to the air. When heated they first melt in their water of crystallisation, leaving the anhydrous salt on further heating, which decomposes at a red heat, glucina remaining behind. In contact with a saturated solution this hydrate passes at about 112° into the dihydrate, which is stable in dry air and melts at 158°, yielding the monohydrate, which loses all its water at

[1] Hahn and van Oordt, *Zeit. anorg. Chem.*, 1904, **38**, 377; van Oordt, German Patent, 165488 (19/12/03).

[2] Humpidge, *Proc. Roy. Soc.*, 1885, **38**, 188; Nilson and Pettersson *Ber.*, 1884, **17**, 987.

[3] Weinland and Schlegelmilch, *Zeit. anorg. Chem.*, 1902, **30**, 134.

[4] Lebeau, *Compt. rend.*, 1898, **126**, 1272, 1418.

220°; a hexahydrate also exists.[1] The sulphate does not form mixed crystals with the sulphates of copper, nickel, iron, &c., and differs in this respect from the sulphates of the magnesium group of metals.[2]

Glucinum readily forms basic sulphates, which are obtained by boiling the normal sulphate with glucinum carbonate or hydroxide; they form gelatinous or gum-like masses, and are probably not definite compounds, but are more probably solid solutions of the hydroxide and sulphate.

Glucinum Nitrate, $Gl(NO_3)_2,3H_2O$, crystallises with difficulty. It is extremely deliquescent, and is easily soluble in alcohol. When heated for twenty hours on the water-bath a thick mass of the basic salt, $Gl(OH)NO_3,H_2O$, is obtained, which is readily soluble in water. On heating to 200° the oxide is produced.

Glucinum Carbide, GlC_2, is obtained by heating glucina with sugar charcoal, and a little oil, to a very high temperature in the electric furnace. It forms transparent yellowish-brown microscopic crystals, which are slowly decomposed by water and dilute acids with evolution of pure methane.[3]

Glucinum Borocarbide, $C_4B_6Gl_6$, is produced when glucina is heated with boron in a carbon boat in the electric furnace. It forms a hard crystalline mass, which is not attacked by water, and is only superficially oxidised when heated in oxygen.[4]

Carbonates of Glucinum.—The normal carbonate, $GlCO_3,4H_2O$, is obtained by passing carbon dioxide for a considerable time through water containing basic carbonate of glucinum in suspension. The solution is allowed to evaporate over sulphuric acid in an atmosphere of carbon dioxide. Crystals are then formed which readily decompose with evolution of carbon dioxide.

When a solution of a glucinum salt is added to an alkali carbonate, or when a solution of the oxide in ammonium carbonate is boiled, a basic carbonate of varying composition separates out as a white powder.

[1] Levi-Malvano, *Zeit. anorg. Chem.*, 1906, **48**, 446; Parsons, *J. Amer. Chem. Soc.*, 1904, **26**, 1433.

[2] Retgers, *Zeit. physikal. Chem.*, 1896, **20**, 481.

[3] Lebeau, *Compt. rend.*, 1895, **121**, 496; Henry, *ibid.*, 600.

[4] Lebeau, *Compt. rend.*, 1898, **126**, 1347.

Detection and Estimation of Glucinum.

284 The salts of this metal do not impart any tint to the non-luminous gas-flame. The glucinum spark spectrum contains two characteristic bright lines in the blue, having a wave-length of 4,573 and 4,489 (Kirchhoff and Thalén). These lines are, however, not seen when the chloride is volatilised in the electric arc (Bunsen).

Glucinum may be readily separated from all other metals by the fact that its oxide is soluble in ammonium carbonate solution. In the process of analysis it is precipitated together with alumina, and it may be separated from this earth by treatment with ammonium carbonate. For quantitative estimation and for separation from alumina and ferric oxide the method proposed by Joy may be employed. The precipitate is treated with ammonium carbonate, the filtrate boiled, and the precipitated basic carbonate of glucinum converted by ignition into the oxide, which is weighed. The metal can also be separated from aluminium by boiling the neutral solution with sodium thiosulphate, which precipitates aluminium hydroxide.[1]

Glucinum can be quantitatively precipitated as hydroxide by ammonia or by a boiling solution of iodate and iodide of potassium (Glassmann).

The Atomic Weight of glucinum has been determined by Nilson and Pettersson[2] by analysis of the sulphate, and found to be 9·04, whilst Krüss and Moraht[3] by the same method found it to be 8·99. Parsons,[4] by the analysis of certain organic derivatives, the acetylacetonate and the basic acetate, has obtained the number 9·1 (O = 16), which is now (1913) adopted as the most probable value.

MAGNESIUM. Mg = 24·32.

285 Nehemiah Grew, a London physician living in the seventeenth century and for some time secretary of the Royal Society, published in the year 1695 an account of a peculiar salt found in the well-known mineral spring at Epsom under the title "*De*

[1] Glassmann, *Ber.*, 1906, **39**, 3366.
[2] *Ber.*, 1880, **13**, 1451.
[3] *Ibid.*, 1890, **23**, 2556.
[4] *J. Amer. Chem. Soc.*, 1904, **26**, 721 ; *Zeit. anorg. Chem.*, 1905, **46**, 215.

salis carthartici in aquis Ebshamensibus et alius contenti natura et usu." The medicinal value of this salt soon afterwards became widely celebrated, and the salt was known in England as Epsom-salts, and on the continent as English-salt. The presence of the same substance was soon afterwards detected in other English mineral springs, and George and Francis Moult in the year 1700 established a large manufactory of the salt near London, obtaining it from a spring at Shooter's Hill. In 1710 Hoy discovered that the same salt could be obtained by crystallisation from the mother-liquors of sea-water after addition of green vitriol (ferrous sulphate). The same salt was subsequently shown by Fr. Hoffmann to exist in the Seidlitz mineral water. Another compound of magnesium having medicinal value was also discovered at the beginning of the eighteenth century by a Roman ecclesiastic, and termed by him *magnesia alba*. Why this name was given to it in contrast to *magnesia nigra*—as black oxide of manganese was then called—is not known. The mode of preparation of this substance was for some years kept secret, until in the year 1707 Valentini, of Giessen, pointed out that magnesia alba could be obtained by boiling down the mother-liquors from the preparation of nitre and igniting the residual products. Shortly afterwards, in 1709, Slevogt, of Jena, prepared the same substance by the precipitation of saltpetre mother-liquors with a fixed alkali. The substance thus obtained was a mixture of calcium carbonate and magnesium carbonate in varying proportions; hence its medicinal action was very variable, and a satisfactory discrimination between lime and magnesia was rendered more difficult. The distinction between these two earths was first clearly pointed out by Black in the year 1755. He showed that white magnesia was a compound of fixed air with a peculiar earth, which differed from lime in yielding a soluble sulphate. The properties of the new earth were subsequently more completely investigated by Bergman in 1775, but Black retained for it the name of magnesia. When Davy proved that this earth was the oxide of a metal, the name of *magnium* was given by him to this metal, the name *magnesium* or *manganesium* being at that time used to designate the metal contained in pyrolusite. This confusion was put an end to by the general adoption of the name magnesium for the metal contained in magnesia alba, and of manganese for that contained in pyrolusite.

Magnesium is a metal widely distributed in nature. It is

found as magnesite, $MgCO_3$; dolomite, $MgCa(CO_3)_2$; kieserite, $MgSO_4,H_2O$; epsomite, $MgSO_4,7H_2O$; kainite, $MgSO_4,K_2SO_4$, $MgCl_2,6H_2O$; carnallite, $MgCl_2,KCl,6H_2O$; spinel, MgO,Al_2O_3; asbestos, $CaMg_3(SiO_3)_4$; talc, $H_2Mg_3(SiO_3)_4$; meerschaum, $H_2Mg_2(SiO_3)_3,H_2O$, and as the chief constituent of many silicates, such as augite, olivine, tourmaline, and serpentine, while it is contained in smaller quantities in most of the other silicates.

Magnesium sulphate, $MgSO_4$, is a chief constituent of certain saline springs, whilst the chloride, $MgCl_2$, occurs in salterns and in sea-water. Magnesium is also found in the animal and vegetable worlds. The bones of animals and the seeds of the cereals contain small quantities of magnesium phosphate, and ammonium magnesium phosphate separates out from urine on standing, thus giving rise to many urinary deposits as well as to gravel and stone. The same salt likewise occurs in guano.

286 *Preparation of Metallic Magnesium.*—Davy was the first to prepare metallic magnesium, but he did not obtain it in the pure state. It was first obtained as a coherent metal by Bussy,[1] who fused the anhydrous chloride of magnesium with potassium. Bunsen afterwards obtained it by the electrolysis of magnesium chloride, which for this purpose was fused in a porcelain crucible[2] (Fig. 162): the carbon of the negative pole was cut so as to form pockets, as shown in Fig. 163, inside which the metal was deposited: unless this precaution was taken, the

Fig. 162.

Fig. 163.

metal, being lighter than the fused chloride, rose to the surface and burned. As it is difficult to prepare the pure chloride, Matthiessen employed a mixture of the chlorides of potassium and magnesium in the ratio of 3 molecules of potassium chloride to 4 of magnesium chloride.[3]

[1] *Journale de Chimie Medicale Ann.*, 1830, 141.
[2] *Annalen*, 1852, **82**, 137.
[3] *Journ. Chem. Soc.*, 1856, **8**, 107.

The manufacture of magnesium on the large scale was first effected by Sonstadt and Mellor. The process employed was essentially that of Caron and Deville,[1] which consisted in heating together magnesium chloride, fluor-spar, and sodium. Wöhler suggested the use of the fused double chloride of magnesium and sodium instead of anhydrous magnesium chloride, whilst Sonstadt introduced the use of fused carnallite. An important improvement was the distillation of the crude metal, as this usually contains carbon, silicon, and nitrogen. The fact that magnesium can be readily distilled was indeed discovered by Deville and Caron, but first technically employed by Sonstadt. For this purpose the crude magnesium was placed in an iron crucible having an iron tube passing through from the bottom to within an inch of the lid. The crucible was filled with the crude metal to the level of the mouth of the tube, the lid carefully screwed and luted down, and the air displaced by a current of hydrogen or coal-gas. As the crucible become heated the magnesium distilled over, passing through the upright tube into a box placed below, where, on the completion of the operation, it was found in the form of a coherent mass which was subsequently melted and cast into ingots or any other form that might be required.

Magnesium is now mainly manufactured by the electrolysis of fused carnallite, which gives up its water of crystallisation and forms a clear fluid below 700° C. The electrolysis is conducted in a closed electric furnace, and a current of coal gas or hydrogen is passed through during the process to remove all oxygen and to carry off the chlorine which is evolved, and thus prevent its action on the metallic magnesium which is set free and floats on the surface of the fused electrolyte. A current density of 0·15 ampère per square centimetre of cathode area is required. The metal is usually pressed when in a semi-fluid state into wire of varying thickness and of any required length; this is afterwards flattened into ribbon, in which form it usually occurs in commerce.

The magnesium industry is quite small, although the increased use of "magnalium" alloys has given it an impetus. These alloys[2] consist of aluminium and magnesium. The alloy containing 10 per cent. of magnesium resembles zinc, that with 15 per cent. resembles brass, and that with 25 per cent. resembles bronze.

[1] *Ann. Chim. Phys.*, 1863, [3], **67**, 347.
[2] *Eng. and Min. Journal*, 1899, **68**, 664.

These alloys give good castings, which can be worked like brass, and are lighter than aluminium.

287 *Properties.*—Magnesium is a brilliant white metal, which melts at 650°, and boils at about 1100°. It has a specific gravity of 1·75, and a granular crystalline fracture, and is sometimes obtained in hexagonal crystals isomorphous with those of cadmium and zinc. It preserves its lustre in dry air, but in moist air becomes covered with a film of oxide; when a piece of ribbon is held in the flame of a candle it burns with an intensely white light, forming a mixture of magnesia and magnesium nitride. The heated metal readily decomposes steam, hydrogen being evolved and magnesia produced. Magnesium also burns readily in carbon dioxide, carbon being deposited. It dissolves easily in dilute acids, and begins to decompose concentrated sulphuric acid at 215°.[1] It is not acted on by alkalis. When the metal is brought into a solution of one of its salts, it slowly dissolves, hydrogen being evolved and the hydroxide or a basic salt being produced.[2] It brings about a similar decomposition in many other salt solutions, producing for example in a solution of copper sulphate a precipitate of copper and cuprous oxide, and an evolution of hydrogen.[3]

Magnesium has been obtained by the electrical method (p. 73) in the form of an olive-green, unstable colloidal solution in ether.[4]

The light from burning magnesium wire is rich in chemically active rays, so that it is possible to photograph by means of it. Bunsen and Roscoe have determined the actinic value of this light compared with that of the sun.[5] They showed that a burning surface of magnesium wire, which seen from a point at sea level has an apparent magnitude equal to that of the sun, effects, at that point, the same chemical action as the sun would do if shining from a cloudless sky at the height of 9° 53′ above the horizon. On comparing the visible brightness of these two sources of light it was found that the

[1] Adie, *Proc. Chem. Soc.*, 1899, 133.

[2] Kippenberger, *Chem. Zeit.*, 1895, **19**, 269; Vitali, *L'Orosi*, 1895, **18**, 289; Lemoine, *Compt. rend.*, 1899, **129**, 291; Bryant, *Chem. News*, 1899, **79**, 75; Kahlenberg, *J. Amer. Chem. Soc.*, 1903, **25**, 380; Roberts and Brown, *ibid.*, 801.

[3] Commaille, *Compt. rend.*, 1866, **63**, 556; Clowes and Caven, *Proc. Chem. Soc.*, 1897, **13**, 221; Divers, *ibid.*, 1898, **14**, 57; Tommasi, *Bull. Soc. chim.*, 1899, [3], **21**, 885.

[4] Svedberg, *Ber.*, 1905, **38**, 3616.

[5] *Phil. Trans.*, 1859, **149**, 920.

brightness of the sun's disc as measured by the eye is 524·7 times as great as that of burning magnesium when the sun's zenith-distance is 67° 22′, whilst at the same zenith-distance the sun's *chemical brightness* was only 36·6 times as great. Hence the value of this light as a source of chemically active rays for photographic purposes becomes at once apparent. The light from burning magnesium has been employed for signalling, and for military and naval purposes, and it is especially employed in pyrotechny. Magnesium powder mixed with an oxidising agent, such as potassium chlorate or a peroxide, is much used for the production of flash lights for photographic purposes.

Metallic magnesium combines with nitrogen on heating, forming the nitride, and has been used for the separation of the argon group of gases from atmospheric nitrogen; it is also made use of in chemical analysis, and in toxicological investigations, where, as it is perfectly free from arsenic, it may be used with advantage in Marsh's apparatus in the place of zinc. It may be used also in the estimation of nitrates and nitrites in drinking water, and in other cases, as a reducing agent. In the form of powder it reduces most metals from their oxides when heated with the latter, and is used for the preparation of several elements such as silicon and boron.[1]

MAGNESIUM COMPOUNDS.

Magnesium and Oxygen.

288 The only stable oxide of magnesium is the monoxide, MgO, with which correspond the salts of the metal. The peroxide, MgO_2, has not been obtained pure, and the existence of the suboxide, Mg_8O_5, is doubtful.[2]

Magnesium Oxide or Magnesia, MgO.—This substance, which occurs as the mineral periclase, is formed when the metal burns in the air, and is also produced by the ignition of the magnesium salt of any volatile oxy-acid. It is prepared on the large scale by igniting the carbonate, magnesia alba, and is known as *magnesia usta* or *calcined magnesia*. Two varieties of this are prepared from the corresponding varieties of the basic carbonate (p. 638), and they are known as light and heavy magnesia, the volumes occupied by equal weights being in the ratio

[1] Winkler, *Ber.*, 1890, **23**, 44, 120.

[2] Baborovsky, *Ber.*, 1903, **36**, 2719; *Zeit. Elektrochem.*, 1905, **11**, 465.

of 3·5 to 1. When brought into water combination takes place and the hydroxide is formed,[1] but the rate at which this combination occurs varies greatly with samples of the oxide which have been prepared by different methods. Thus the oxide prepared by gently heating the native carbonate or the nitrate sets with water to a firm mass, whilst the light and heavy oxides combine rapidly but do not set, and crystals of the hydroxide are scarcely attacked by water.[2] It is tasteless, but in the moist state turns red litmus paper blue. When heated in an electric furnace it forms transparent crystals, melts at about 2250°, and finally volatilises, though less readily than lime. Reduction to magnesium and magnesium carbide takes place when the oxide and carbon are heated in the electric furnace.[3] When magnesia is ignited in a current of hydrogen chloride it is obtained in the form of regular cubes and octahedra, and if a mixture of magnesia and ferric oxide is treated in this way black octahedra of magnoferrite, MgO,Fe_2O_3, are formed, together with those of MgO containing a little ferric oxide; these are of a yellow colour, identical with periclase, a mineral found at Monte Somma, near Naples. Crystals resembling those of periclase are also formed when the hydroxide is heated to redness with caustic potash.[4]

Magnesia is employed as a medicine, as a refractory lining in furnaces, for the manufacture of crucibles,[5] and in certain processes for the regeneration of chlorine from ammonium chloride.

Magnesium Hydroxide, $Mg(OH)_2$, is obtained as a white precipitate when aqueous potassium or sodium hydroxide is added to a solution of a magnesium salt, and occurs in nature as the mineral brucite, which is found embedded in serpentine with other magnesium minerals. It has been found by the conductivity method that it dissolves in 115,000 parts of water at 18° (8·7 milligrams per litre), but direct determinations give higher numbers.[6] The hydroxide can be dried at 100° without loss of water, but is converted into the oxide at a low red heat. The hydroxide is not precipitated from solutions of magnesium salts by ammonia in presence of ammonium salts, this being

[1] Rose, *Pogg. Ann.*, 1851, **83**, 450.
[2] See also Anderson, *Journ. Chem. Soc.*, 1905, **87**, 257.
[3] Lebeau, *Compt. rend.*, 1907, **144**, 799.
[4] de Schulten, *Bull. Soc. Fran. Min.*, 1898, **21**, 87.
[5] See *Chem. Zeit.*, 1906, **30**, 211, 329.
[6] Dupré, junr., and Bialas, *Zeit. angew. Chem.*, 1903, **16**, 54.

probably due to the fact that the presence of these salts greatly diminishes the dissociation of the molecules of $NH_4.OH$ present in aqueous ammonia (p. 137).[1]

Magnesium Peroxide.—When caustic soda is added to a solution of magnesium sulphate containing hydrogen peroxide, the precipitate contains a peroxide of magnesium, which has, however, not been prepared pure. The material obtained gradually loses oxygen when preserved, and after drying appears to contain about equal molecular proportions of the oxide and peroxide.[2] The commercial product usually contains about 8 per cent. of available oxygen.[3] Carrasco[4] has obtained the following peroxides by successive addition of an ethereal solution of hydrogen peroxide to magnesia: $5MgO,2MgO_2,3H_2O$; $3MgO,2MgO_2,3H_2O$, and $2MgO,2MgO_2,3H_2O$. They are light powders which explode violently when heated.

Magnesium and the Halogens.

289 *Magnesium Fluoride*, MgF_2, occurs as the mineral sellaïte in colourless tetragonal crystals, found at Montiers in Savoy. When pure magnesia is evaporated to dryness with an excess of aqueous hydrofluoric acid, this same compound is obtained as an amorphous mass almost insoluble in water. When this is fused with common salt and the mass gradually cooled, it is deposited in crystals which, after washing with water, exhibit the same form as sellaïte (Cossa).

Magnesium Chloride, $MgCl_2$, is contained in sea-water, in many brine springs, and in various salt beds, and is at present prepared in large quantities at Stassfurt. It forms several crystalline hydrates, the limits of stability of which in contact with a saturated solution are as follows: $12H_2O$ from $-33{\cdot}6°$ to $-16{\cdot}8°$, the melting point being $-16{\cdot}4°$; $8H_2O(\alpha)$ from $-16{\cdot}8°$ to $-3{\cdot}4°$; $6H_2O$ from $-3{\cdot}4°$ to $116{\cdot}7°$; $4H_2O$ from $116{\cdot}7°$ to $181{\cdot}5°$; above this temperature $2H_2O$. In addition to these, an isomeric labile hydrate with $8H_2O$ (β) is known.[5] 100

[1] Lovén, *Zeit. anorg. Chem.*, 1896, **11**, 404; Treadwell, *Zeit. anorg. Chem.*, 1904, **37**, 326.

[2] Ruff and Geisel, *Ber.*, 1904, **37**, 3683.

[3] Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, **25**, 298. See also German Patent, No. 168271 (27/7/1901).

[4] *Gazz.* 1909, **39**, ii., 47.

[5] van't Hoff and Dawson, *Zeit. physikal. Chem.*, 1897, **22**, 598; van't Hoff and Meyerhoffer, *ibid.*, 1898, **27**, 75; Bogorodsky, *J. Russ. Chem. Phys. Soc.*, 1898, **30**, 735.

parts of water dissolve 53·5 parts of anhydrous salt at 10°, 73 parts at 100°, and 128 parts at 186°. The hydrate with $6H_2O$, which is deposited when a hot concentrated solution cools, crystallises in deliquescent needles, and is decomposed on heating above 186°, water and hydrochloric acid being given off, and magnesia remaining. The anhydrous salt can be obtained by heating this hydrate to 175° in a vacuum [1] or by adding ammonium chloride to the solution, evaporating to dryness, carefully heating and finally igniting. It may also be obtained by evaporating the solution in a current of hydrochloric acid gas (Hempel), and forms a laminated crystalline solid, which dissolves in water with evolution of heat. It possesses a bitter saline taste, and is now largely used for the purpose of dressing cotton goods. Magnesium chloride forms crystalline double salts with other chlorides, especially with those of the alkaline earths. Of these the following are the most important:

Potassium Magnesium Chloride or Carnallite, $MgCl_2,KCl,6H_2O$. —This compound crystallises in rhombic prisms which deliquesce on exposure to the air, leaving a residue of potassium chloride.

Ammonium Magnesium Chloride, $MgCl_2,NH_4Cl,6H_2O$, is deposited from solution in small rhombic crystals which dissolve in six parts of water.

Calcium Magnesium Chloride or Tachhydrite,

$$2MgCl_2,CaCl_2,12H_2O,$$

occurs at Stassfurt in yellowish rounded masses which deliquesce on exposure to the air. It can readily be prepared by dissolving the constituent salts in a liquid containing 1,000 molecular proportions of water, 44 of magnesium chloride, and 106 of calcium chloride, and cooling to 25°.[2]

Oxychlorides of Magnesium.—If strongly ignited magnesia be brought into contact with a concentrated solution of the chloride, the mixture after standing for some hours solidifies to a mass so hard that it is capable of being polished (Sorel). A mass of this kind which had been exposed for six months to the air gave results on analysis which render it probable that it is a mixture of magnesium carbonate and the compound

$$MgCl_2,5MgO,17H_2O, \text{ or } 2Mg\begin{cases}Cl\\OH\end{cases},4Mg(OH)_2,12H_2O.$$

This substance loses water on heating, but does not give off

[1] German Patent, 161662 (7/3/03).

[2] van't Hoff, *Zeit. anorg. Chem.*, 1905, **47**, 271.

hydrogen chloride, and chloride of magnesium may be withdrawn from it by repeatedly boiling with water, leaving a residue of magnesium hydroxide as a hard non-crystalline mass resembling brucite.[1] If a solution of magnesium sulphate to which ammonia and sal-ammoniac have been added (a mixture frequently used in the laboratory) is allowed to stand for some time, a crystalline precipitate having the composition $2Mg\begin{cases}OH\\Cl\end{cases},4Mg(OH)_2,8H_2O$ is sometimes formed (J. Davis).

Magnesium Bromide, $MgBr_2$, occurs in sea-water and in many brine springs. The anhydrous salt is obtained by heating magnesium in bromine vapour, or by leading bromine vapour over an ignited mixture of magnesia and sugar charcoal. It forms a white crystalline mass which hisses and evolves heat when brought into contact with water, and crystallises from a hot concentrated solution in needles, having the composition $MgBr_2,6H_2O$. At 18° the saturated solution contains 103·4 parts of the anhydrous salt dissolved in 100 of water.[2] On heating the crystals, hydrobromic acid is given off and magnesia is left behind.[3] The bromide, like the chloride, forms many double salts,[4] and also combines with many organic substances.

Magnesium Iodide, MgI_2, is found together with the bromide in sea-water and brine springs. It can be prepared by dissolving magnesia in hydriodic acid. On evaporation, hygroscopic crystals of the hydrate, $MgI_2,8H_2O$, are deposited, which readily undergo decomposition with liberation of iodine. The solution saturated at 18° contains 148 parts of the anhydrous salt dissolved in 100 of water (Mylius and Funk).

Magnesium and Sulphur.

290 *Magnesium Sulphide*, MgS.—This substance is not formed in the wet way, but is obtained when a mixture of magnesium filings and sulphur is heated to dull redness in a current of sulphur vapour[5] or sulphuretted hydrogen. The product is a brown, coherent, hard, and brittle coke-like mass, mixed with a small quantity of magnesium oxide and some unchanged metal. On exposure for some time to the air the difficultly

[1] Bender, *Annalen*, 1871, **159**, 341.
[2] Mylius and Funk, *Ber.*, 1897, **30**, 1716.
[3] See Kreider, *Amer. J. Sci.*, 1905, (4), **20**, 97.
[4] de Schulten, *Bull. Soc. chim.*, 1897, (3), **17**, 167.
[5] Parkinson, *Journ. Chem. Soc.*, 1867, **20**, 127.

fusible sulphide slowly tarnishes, and evolves sulphuretted hydrogen, and the granular and bright steel-grey fracture becomes dull and coated with a grey oxide. When heated in the electric furnace[1] it forms cubical crystals of sp. gr. 1·85. It is slightly soluble in water, yielding a straw-yellow solution, but on exposure to the light it deposits sulphur and becomes colourless. This solution doubtless contains magnesium hydrosulphide, $Mg(SH)_2$, which may also be obtained by passing sulphuretted hydrogen into water containing magnesia in suspension.[2] It is an extremely unstable compound, and on exposure to the air, or when heated, gives off sulphuretted hydrogen, leaving magnesia behind. A solution of this substance has been proposed as a source of sulphuretted hydrogen for laboratory purposes.

Magnesium Sulphate, $MgSO_4$, occurs in nature as *kieserite*, $MgSO_4,H_2O$, and *Epsom salts* or *epsomite*, $MgSO_4,7H_2O$. These two compounds can be readily distinguished by the action of water on them. Epsom salts is readily soluble in water, whilst kieserite is as sparingly soluble as gypsum. Kieserite occurs crystallised in rhombic prisms, but is more commonly found in granular masses which dissolve slowly when allowed to remain in contact with water, being gradually converted into Epsom salts. Epsom salts occur in many mineral waters. The same compound is found as epsomite or hair-salt in silky fibres and fibrous crusts at Idria in Carniola, in the gypsum quarries of Montmartre near Paris, and in various other localities. The floors of the limestone caves in Kentucky, Tennessee, and Indiana are in many instances covered with minute crystals of epsomite mingled with earth. In the Mammoth cave in Kentucky it adheres in loose masses like snowballs (Dana).

The manufacture of magnesium sulphate from the upper layers of salt (*Abraumsalz*) at Stassfurt is carried out on the large scale. The crude kieserite is placed in sieves in water. The magnesium chloride and finely divided chloride of sodium dissolve, whilst the kieserite falls through the meshes of the net in small powder, and larger pieces of rock-salt, anhydrite, and earthy impurities remain behind. The powder is then brought into conical wooden moulds in which it is allowed to remain, and in which it soon becomes a hard coherent mass, inasmuch

[1] Mourlot, *Compt. rend.*, 1898, **127**, 180.
[2] Berzelius, *Pogg. Ann.*, 1825, **6**, 443.

as a portion of the salt combines with water to form the heptahydrate, which binds together the remaining powder of the kieserite. This kieserite-stone is then dried and powdered, and contains 80 to 90 per cent. of magnesium sulphate, and from 1 to 2 per cent. of common salt. It is either brought into the market in this form, or worked up into Epsom salts. Sulphate of magnesium was formerly produced in considerable quantity by treating either native magnesium carbonate or dolomite with sulphuric acid; the gypsum formed in the latter case, being much less soluble than magnesium sulphate, is easily separated from it. Formerly, also, dolomite was burnt, the lime dissolved out by crude pyroligneous acid, and the residual magnesia treated with sulphuric acid (Henry).

Magnesium sulphate forms a large number of hydrates, but the curve of equilibrium with a saturated solution has not been very accurately determined. The ordinary heptahydrate (Epsom salts) is stable in contact with a saturated solution from 1·8° to 0·48°, at which temperature it passes into the hydrate with $6H_2O$, which in its turn passes into kieserite at 68°. The heptahydrate crystallises from a hot concentrated solution in four-sided rhombic prisms (Class 6, p. 201), shown in Fig, 164, and is isomorphous with the corresponding sulphates of zinc and nickel. As a rule, the commercial salt occurs in the powdery form consisting of minute delicate needles obtained by quick crystallisation of a concentrated solution. The crystals are not deliquescent, but the commercial salt sometimes becomes moist in contact with air in consequence of the presence of traces of magnesium chloride. The crystals possess an unpleasant saline bitter taste, and have a specific gravity of 1·685 (Schiff). On heating, they melt in their water of crystallisation, and lose six molecules at 150°, the last molecule being termed by Graham *constitutional water*, because it is not driven off until a temperature of 200° is reached. The solution saturated in contact with this hydrate at 10° contains 30·9 parts of anhydrous salt in 100 of water, and at 40°, 45·6 parts.

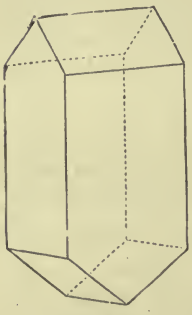


Fig. 164.

When a boiling and concentrated solution of magnesium sulphate is placed in a closed vessel it remains supersaturated when cold. Such a solution may stand for weeks or months

without solidification, but milk-white crystals of the hexahydrate are sometimes deposited, and, sometimes, monoclinic tablets of a labile heptahydrate. From this it is seen that the heptahydrate is dimorphous; this is shown also by the fact that it crystallises as an isomorphous constituent with monoclinic ferrous sulphate, $FeSO_4,7H_2O$. Magnesium sulphate is insoluble in absolute alcohol.

Epsom salts is largely used as a purgative, and, like the chloride, is employed as a dressing for cotton goods. It is also used in dyeing with aniline colours, as goods thus dyed are found to stand the action of soap better, this being probably due to the formation of an insoluble magnesia soap.

Magnesium sulphate forms a series of characteristic double salts with the sulphates of the alkali metals. These have the general formula $MgSO_4,M^I_2SO_4,6H_2O$, and crystallise in well-developed monoclinic prisms.[1] It also forms a large number of other double salts, many of which occur as minerals. When the anhydrous sulphate is dissolved in hot concentrated sulphuric acid, the solution on standing deposits the compound $MgSO_4,H_2SO_4$, in six-sided tablets, which soon absorb moisture from the air and are thereby decomposed.[2]

Magnesium and Nitrogen, Phosphorus and Arsenic.

291 *Magnesium Nitride*, Mg_3N_2.—Deville and Caron, when preparing magnesium, observed that the distilled metal sometimes appeared covered with small transparent needles,[3] which decomposed in moist air with formation of ammonia and magnesia, and therefore contained a nitride of magnesium. This compound was obtained in the amorphous state by Briegleb and Geuther,[4] by igniting magnesium in ammonia or in nitrogen gas. The nitride of magnesium thus prepared is a greenish-yellow amorphous mass, which when heated in dry oxygen gas is converted, with bright incandescence, into magnesia. The nitride is, however, produced when compressed magnesium turnings are burnt in the air, and is covered by a layer of oxide.[5] On exposure to the air, or when treated with water, it

[1] See Tutton, *Journ. Chem. Soc.*, 1896, **69**, 355; 1905, **87**, 1123.
[2] Schiff, *Annalen*, 1861, **118**, 365.
[3] *Ann. Chim. Phys.*, 1863, [3], **67**, 348.
[4] *Annalen*, 1862, **123**, 228; see also Merz, *Ber.*, 1891, **24**, 3940.
[5] Kirchner, *Chem. Zeit.*, 1901, **25**, 395.

is quickly decomposed into ammonia and magnesia, so much heat being evolved in the latter case that the water boils. When heated in a current of sulphuretted hydrogen gas ammonium sulphide and magnesium sulphide are formed.

Magnesium Nitrate, $Mg(NO_3)_2$.—This salt occurs in the mother-liquors from the saltpetre manufacture, and in the surface water of towns, having been first detected by Berzelius in the well-water of Stockholm. It is prepared by dissolving magnesia alba in nitric acid. It forms several hydrates,[1] that with $9H_2O$ being stable in contact with a saturated solution from $-29°$ to $-18°$, at which temperature it passes into the hexahydrate, which crystallises in prisms and needles and melts at 90°. The solution saturated at 18° contains 73·4 parts of the anhydrous salt in 100 parts of water. The hexahydrate dissolves in nine parts of alcohol of specific gravity 0·84, but is less soluble in pure alcohol.

Magnesium Phosphide, Mg_3P_2, is formed in small, dark-coloured crystals, when magnesium is heated in hydrogen containing phosphorus vapour. It is decomposed by water with formation of magnesium hydroxide and pure phosphine, and burns in oxygen, forming magnesium phosphate.[2]

Phosphates of Magnesium.—The Normal Orthophosphate, $Mg_3(PO_4)_2$, occurs in small quantities in the seeds of the cereals and in bones. It is obtained in the form of a hydrated white precipitate when a solution of normal sodium orthophosphate is added to a solution of Epsom salts.[3] One part of the salt dissolves in 5,000 parts of water. A phosphato-fluoride of magnesium having the formula $2Mg_3(PO_4)_2,MgF_2$ occurs in nature as *wagnerite*.

Hydrogen Magnesium Orthophosphate, $HMgPO_4$, is obtained when a solution of Epsom salts is mixed with one of common sodium phosphate; on standing, hexagonal needles of the acid salt containing seven molecules of water are deposited. These dissolve in 322 parts of cold water. If this solution is heated it becomes milky owing to the separation of the insoluble normal salt, a tetra-hydrogen phosphate, $H_4Mg(PO_4)_2$, remaining in solution; this latter compound, however, has not been obtained in the pure state. A hydrate with $3H_2O$ has also been described.[4]

[1] Funk, *Ber.*, 1899, **32**, 96; Mylius and Funk, *Ber.*, 1897, **30**, 1716.

[2] Gautier, *Compt. rend.*, 1899, **128**, 1167.

[3] See de Schulten, *Bull. Soc. chim.*, 1903, (3), **29**, 724; *Bull. Soc. Fran. Min.*, 1903, **26**, 81.

[4] Struve, *Zeit. anal. Chem.*, 1897, **36**, 289.

Magnesium Ammonium Orthophosphate, $Mg(NH_4)PO_4,6H_2O$. —This salt, a frequent constituent of urinary calculi, was discovered by Fourcroy. It is produced in the putrefaction of urine, and large crystals of it have been found in some varieties of guano. It is formed when an ammoniacal solution of sal-ammoniac is mixed with a solution of magnesium sulphate, and a soluble orthophosphate then added. If the solution be dilute, the precipitate takes some time to form, and deposits in small crystals which attach themselves to the sides of the vessel, especially upon points presenting any roughness or inequality, as where the beaker-glass has been scratched. It separates in this way from extremely dilute solutions, affording a very delicate test either for magnesium or for phosphoric acid. According to Graham the best mode of obtaining it in distinct crystals is to mix 600 parts of hot water with four parts of strong ammonia; then add seven parts of crystallised sodium phosphate, two parts of sal-ammoniac, and four parts of magnesium sulphate. The crystals which are thus deposited are transparent tetragonal prisms. One part of the salt dissolves in 15,000 parts of water at 15°, and in 44,000 parts of ammoniacal water, whilst in presence of ammonium chloride it is somewhat more readily soluble. When heated the salt gradually loses the whole of the water and ammonia, pyrophosphate of magnesium, $Mg_2P_2O_7$, remaining behind.[1]

The Arsenates of Magnesium closely correspond to the phosphates.

Magnesium and Carbon and Silicon.

292 *Carbides of Magnesium.*—Two carbides of magnesium, MgC_2 and MgC_3, exist. The first yields acetylene when treated with water, and the second allylene. They have not been prepared pure.[2]

Carbonates of Magnesium.—Normal Magnesium Carbonate, $MgCO_3$, occurs in nature as magnesite, a mineral isomorphous with calc-spar. The same mineral frequently occurs in compact or granular masses, and is found in large quantities in various localities, especially in the island of Eubœa. The normal carbonate is also formed by the action of magnesium chloride on calcium carbonate (Marignac). It has a specific gravity of

[1] Compare Struve, *Zeit. anal. Chem.*, 1898, **37**, 485.

[2] Novák, *Zeit. physikal. Chem.*, 1910, **73**, 513.

3·056, is not easily soluble in dilute acid, and is not affected by being boiled with water or alkali carbonates.

A second variety of the normal carbonate is obtained by heating magnesium ammonium carbonate in dry air at 130°. It differs remarkably from magnesite in its properties, as it is very hygroscopic, and when treated with water sets like plaster of Paris to a hard mass[1] consisting of the hydroxycarbonate. Magnesium carbonate readily dissolves in carbonic acid, but the solution is only stable in presence of excess of carbon dioxide.[2] The amount dissolved increases with the pressure of the carbon dioxide and diminishes with rise of temperature.

According to Engel,[3] 1,000 parts of water at 12° contain the following amounts of magnesium carbonate in the form of bicarbonate when saturated under varying pressures of carbon dioxide:

Pressure of CO_2 . .	0·5	1	1·5	2	2·5	3	6 atmospheres.
Parts of $MgCO_3$ as $Mg(CO_3H)_2$ . .	20·5	26·5	31	34·2	36·4	42·8	50·6

The solution has an alkaline reaction and a bitter taste. If it be placed in a partially closed flask at 50°, crystals of the empirical formula $MgCO_3,3H_2O$ separate out, and a similar change occurs when the solution is heated. This substance is probably the *hydroxycarbonate*, $HO{\cdot}Mg{\cdot}CO_3H,2H_2O$, for it loses $2H_2O$ at 100°, but does not begin to lose carbon dioxide or the remaining molecule of water until 125° is reached. Crystals of the empirical formula $MgCO_3,5H_2O$ are deposited at a lower temperature, and these lose $2H_2O$ at 16°. The anhydrous compound, $HO{\cdot}Mg{\cdot}CO_3H$, can also be obtained by boiling the crystals containing $2H_2O$ with xylene. The hydrate is slowly decomposed by boiling water with formation of a mixture of the anhydrous compound and magnesium hydroxide,[4] the composition of which depends on the time of boiling. The hydrated hydroxycarbonate is also formed when a solution of a magnesium salt is precipitated with an equivalent amount of sodium carbonate in the cold. It appears probable that a mixed carbonate[5] of magnesium and sodium is first formed:

$$2Na_2CO_3 + MgSO_4 = Mg(CO_3Na)_2 + Na_2SO_4.$$

[1] Engel, *Compt. rend.*, 1889, **129**, 598.

[2] Treadwell and Reuter, *Zeit. anorg. Chem.*, 1898, **17**, 170.

[3] *Compt. rend.*, 1888, **100**, 444.

[4] Davis, *J. Soc. Chem. Ind.*, 1906, **25**, 788.

[5] See Reynolds, *Journ. Chem. Soc.*, 1898, **73**, 264; von Knorre, *Zeit. anorg. Chem.*, 1903, **34**, 260.

This then immediately undergoes partial hydrolysis into the hydroxycarbonate or a mixture of this and the hydroxide, and the various so-called basic carbonates of magnesium[1] are all to be regarded as mixtures of this kind (Davis). The *magnesia alba* of the shops is a product of variable composition. The "light" variety is prepared by precipitating a dilute solution of Epsom salts in the cold with sodium carbonate, washing with boiling water, and drying at 100°. The "heavy" variety is obtained by adding sodium carbonate solution to a boiling concentrated solution of Epsom salts, evaporating to dryness, digesting with water, filtering and washing, and finally drying at 100°.

When evaporated to dryness, the solution of the carbonate in carbonic acid yields a crystalline powder, which, examined under the microscope, is found to consist of crystals having the form of aragonite;[2] but if the solution is heated to 300° in a vessel closed by a porous stopper through which the carbonic acid can slowly escape, microscopic rhombohedra of the form of native magnesite are deposited.[3] Magnesium carbonate is, therefore, isodimorphous with calcium carbonate.

Another method of preparing magnesium carbonate is that patented by Pattinson, which consists in igniting dolomite and then treating it with water and carbon dioxide under pressure, when the carbonate of magnesium dissolves in the carbonic acid more readily than the carbonate of calcium; the solution of bicarbonate of magnesium which is formed is decanted from the insoluble carbonate of calcium and decomposed by a current of steam. The salt thus obtained is very white and of a loose texture.

The mineral termed *hydromagnesite*, possessing a similar composition to magnesia alba, occurs in small white monoclinic crystals.

Magnesia alba is almost insoluble in water. It dissolves, however, readily in solutions of ammoniacal salts, owing to the formation of ammonium carbonate, and soluble double carbonates of magnesium and ammonium. For this reason ammonium carbonate does not precipitate a magnesium salt completely, and no precipitate occurs in the presence of ammonium chloride.

[1] Brill, *Zeit. anorg. Chem.*, 1905, **45**, 275; Anderson, *Journ. Chem. Soc.*, 1905, **87**, 261.

[2] Rose, *Pogg. Ann.*, 1837, **42**, 366.

[3] Sénarmont, *Ann. Chim. Phys.*, 1850, [3], **30**, 129.

Magnesium Calcium Carbonate or Dolomite, $MgCO_3,CaCO_3$, occurs as a mineral in the massive state, forming whole mountain ranges. It was at one time considered to be an isomorphous mixture of the two constituent carbonates, but it has been found that it possesses a lower degree of crystalline symmetry (Class 15, p. 201) than calcite, and that its properties are not the mean of those of its constituents.

Magnesium Silicide.—This compound was obtained by Wöhler as a by-product in the preparation of metallic magnesium, by fusing together a mixture of sodium, magnesium chloride, and sodium silicofluoride, and was prepared by Geuther by heating sodium chloride, sodium silicofluoride and magnesium to a high temperature in a Hessian crucible.[1] It is most readily obtained by heating 1 part of quartz sand and 1·5 parts of magnesium powder, and then forms a bluish half-fused mass,[2] but when obtained by Geuther's method it forms crystals having a metallic lustre. It has probably the formula Mg_2Si, although Wöhler found the composition Mg_4Si_3, and Geuther Mg_5Si_3. This variation in the results is probably due to the fact that the product readily loses magnesium on ignition,[3] or the substances may be mixtures of Mg_2Si and MgSi. In favour of the latter view is the fact that when the silicide is treated with hydrochloric acid, spontaneously inflammable silicon hydride is evolved, and silicoformic anhydride produced (Vol. I., p. 899), the decompositions being represented thus:

(1) $Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$.
(2) $2MgSi + 3H_2O + 4HCl = 2MgCl_2 + Si_2H_2O_3 + 4H_2$.

The silicide obtained by heating together 48 parts of magnesium and 28 of silicon[4] yields a certain proportion of the silicon hydride, Si_2H_6, when treated with hydrochloric acid, and therefore probably contains a silicide of the formula Mg_3Si_2.

Magnesium Silicates.—As already mentioned (p. 625), magnesium occurs as a constituent of a very large number of silicates, many of which have received important technical applications. For a description of these various minerals reference must be made to works on mineralogy.[5]

[1] *J. pr. Chem.*, 1865, **95**, 424.
[2] Gattermann, *Ber.*, 1889, **22**, 186.
[3] Winkler, *Ber.*, 1890, **23**, 2642.
[4] Moissan and Smiles, *Compt. rend.*, 1902, **134**, 569.
[5] See Miers, *Mineralogy*, Sections XV. and XVI. (London, Macmillan & Co., 1902).

Detection and Estimation of Magnesium.

293 Magnesium and its compounds do not impart any tint to the non-luminous gas-flame. The spark spectrum of magnesium is, however, very characteristic (Bunsen, Kirchhoff, Thalén), giving lines in the green coincident with Fraunhofer's *b*. The brightest of these lines is situated very close to an air-line, and for this reason it is better to observe the magnesium spark in an atmosphere of hydrogen, or in one of coal-gas, than in the air (Bunsen).

In the course of ordinary qualitative analysis, magnesium is obtained together with the alkali metals, as it is not precipitated by ammonium carbonate in presence of ammonium chloride. The presence of magnesium is readily detected by the addition of sodium phosphate to a portion of the solution, as on standing for a short time a crystalline precipitate of $Mg(NH_4)PO_4,6H_2O$ is deposited. The formation of this precipitate is greatly accelerated by stirring the solution with a glass rod, when the crystals are deposited where the rod has scratched the glass.

Magnesium is usually estimated by precipitation as magnesium ammonium phosphate by means of sodium phosphate in the presence of ammonia and ammonium chloride. The precipitate is washed with dilute ammonia, in which it is less soluble than in pure water, and is then converted by ignition into the pyrophosphate, which is weighed. The quantitative separation of magnesium from the alkalis is accomplished by the method proposed by Berzelius. The solution, which must contain the metals in the form of chlorides, as is indeed always the case in the analysis of silicates, &c., is evaporated to dryness, and the residue ignited in order to volatilise the ammoniacal salts. The fixed residue is then warmed with a small quantity of water, and a little finely divided oxide of mercury added, the mixture again evaporated to dryness on a water-bath, and the residue ignited in order to expel the mercuric chloride and excess of oxide. The residue contains the magnesium in the form of the insoluble oxide, whilst the alkali metals remain as chlorides, which are extracted by water and estimated. The precipitation of the magnesia can also be effected by means of baryta water, the excess of baryta being subsequently removed by treatment with carbon dioxide. The magnesia, after having been well washed, is

dissolved in hydrochloric acid, and precipitated as the ammonium magnesium phosphate.

The Atomic Weight of magnesium was very carefully determined by Marignac [1] by the analysis and synthesis of magnesium sulphate, the average number obtained being 24·20. Burton and Vorce,[2] by converting a known weight of pure magnesium into magnesia, obtained the number 24·10, whilst Richards and Parker,[3] by the analysis of the anhydrous chloride, prepared by heating ammonium magnesium chloride, $NH_4Cl,MgCl_2$, in dry hydrogen chloride, obtained the value 24·32, which is at present (1913) accepted.

ZINC. Zn = 65·37.

294 The ancients were acquainted with the alloy of zinc and copper which we term brass, but they were not aware that it contained any other metal besides copper, and it was only after some time that a more accurate examination of brass and the ores which were employed for its production led to the recognition of zinc as an elementary body. Aristotle, in the fourth century B.C., mentions the preparation of brass under the name of Mossinœcian copper, which he describes as being bright and light-coloured, not produced by the addition of tin, but by its having been melted with a peculiar earth found on the shores of the Black Sea. The early use of brass is clearly proved by the following analysis by Tookey, quoted by Percy, of an undoubtedly genuine Greek coin of Trajan struck in Caria A.D. 110 :—

Copper	77·59
Zinc	20·70
Tin	0·39
Iron	0·27
	98·95.

This ore, by means of which copper could be coloured yellow, was termed Καδμεία or *cadmia*, by Dioscorides and Pliny. The same word is also used by the latter author to designate the

[1] *Jahresb.*, 1883, 42. [2] *Amer. Chem. J.*, 1892, **12**, 219.
[3] *Zeit. anorg. Chem.*, 1896, **13**, 81.

sublimate, consisting of impure oxide of zinc, found in the brassfounders' furnaces. It has already been stated in the Historical Introduction that the older alchemists were acquainted with the means of turning copper a yellow colour. The material by which this change was brought about was termed in the Latin translation of their works *tutia*. Agricola believed that brass was a mixture of copper and earth termed galmei or calamine, and he describes the employment of cadmia in the place of the natural ore as follows: "Sunt qui in cadmiæ fossilis locum cadmiam fornacum substituunt."

The word zinc is first found in the writings of Paracelsus, who also pointed out that zinc was a metal. He says in his treatise on minerals: "There is another metal called the *zinken*, which is unknown to the fraternity, and is a metal of a very singular kind." In other places he describes it as a bastard or semi-metal. The word zinc occurs in many subsequent authors, and sometimes it is employed to denote the metal, at other times the ore from which the metal is obtained. Libavius was the first to investigate the properties of zinc more exactly, although he was not aware that the metal was derived from the ore known as calamine. He states that a peculiar kind of tin is found in the East Indies called calaëm. Some of this was brought to Holland, and came into his hands. He describes its outward appearance and general properties minutely, and compares them with those of the other metals, laying very particular stress upon the fact that when heated in the air this metal takes fire and burns. The exact nature of zinc and its ores continued doubtful during the seventeenth century. Glauber, it is true, stated that calamine was an ore of zinc, but Lemery so late as 1675 believed that zinc was identical with bismuth, and Boyle often employed the names zinc and bismuth indiscriminately for the same substance, also using the word spiauter (our English spelter), a name apparently of Eastern origin. In general it was believed that the brass which was obtained from copper and calamine contained the latter substance as such. The view that brass is an alloy was first put forward by Kunkel at the end of the seventeenth century. He says in his *Laboratorium*, "I have already remarked in my annotations that calamine allows its mercurial (metallic) part to pass into the copper and form brass. For thou wilt never believe that as a *sal* it could tinge copper; as a *terra* it cannot enter it, since it would make the copper brittle, and moreover could not tinge.

it." Stahl afterwards gave it as his opinion that calamine could turn copper into brass by being first converted into zinc.

According to W. Hommel,[1] the name zinc is erroneously attributed to Basil Valentine and the discovery of the metal to Paracelsus, for the identification of zinc as the metal from blende was only accomplished by Homberg in 1695.

The preparation of zinc on the large scale appears to have been first carried out in England. According to Bishop Watson, zinc works were first established at Bristol about the year 1743. "In about the year 1766 Watson visited Mr. Champion's works near Bristol and saw the process of making zinc, which at that time was kept rigidly secret. Many years afterwards he published an accurate description of this process, which is the same as that hereafter described as the English process" (Percy).[2] The first Continental zinc works were erected in 1807 at Liége.

Zinc is said to have been found in the native state near Melbourne, in Australia, but it occurs chiefly as zinc blende or zinc sulphide, ZnS, which, when of a yellow colour, is known as rosin-blende, and when of a dark colour as black-jack. It is found in England, in many districts in Europe and America, and also in New South Wales. Another ore which was formerly of chief importance is calamine, smithsonite or zinc-spar, $ZnCO_3$, found near Altenberg, in the neighbourhood of Aix-la-Chapelle, at Wiesloch, in Belgium, Spain, Siberia, and North America, as well as at Alston Moor, Lead Hills, Donegal, and Matlock in Great Britain and Ireland. It also occurs as siliceous or electric calamine, or hemimorphite, Zn_2SiO_4,H_2O, found together with zinc-spar.

Other ores of zinc are franklinite, $(Zn,Fe,Mn)O,(Fe,Mn)_2O_3$; red zinc ore, or oxide of zinc, which derives its peculiar colour from the presence of oxide of manganese; hydrozincite, $ZnCO_3,2Zn(OH)_2$; aurichalcite, $2(Cu,Zn)CO_3,3(Cu,Zn)(OH)_2$; zinc sulphate or goslarite, $ZnSO_4,7H_2O$, and gahnite or zinc-spinel, ZnO,Al_2O_3, &c. Zinc has been found in the ashes of the yellow pansy (*Viola calarminaris*), and of many other plants growing in soil which contains zinc.[3]

295 *Smelting of Zinc.*—In former times calamine was the only ore of zinc from which the metal was extracted, but at the present time large quantities of zinc silicate, a mineral

[1] *Chem. Zeit.*, 1912, **36**, 905. [2] *Metallurgy*, i., 521.
[3] See also Javillier, *Bull. Sci. Pharm.*, 1908, **15**, 559.

occurring with the carbonate, are employed for the preparation of zinc, whilst zinc blende is the chief source. In America the metal is extracted from franklinite and from the red zinc ore. The first process in the preparation of zinc usually consists in the roasting of the ore in order to drive off the carbonic acid and water which it contains, and, in the case of zinc blende, to convert the sulphide into oxide. In roasting the latter ore great care has to be taken to prevent the formation of zinc sulphate, a salt which requires a very high temperature for its decomposition, and which, if not decomposed, would be again converted, in the process of reduction which follows, into sulphide, and thus cause a considerable loss.

This roasting may take place in simple shaft or reverberatory furnaces, but large mechanical furnaces are now being used, these being either revolving furnaces, long-bedded furnaces with mechanical stirrers, or muffle furnaces, also worked mechanically. Blende is sometimes roasted in a Hasenclever furnace, which is of the muffle type, but so arranged that the sulphur dioxide evolved may be used in the manufacture of sulphuric acid.[1]

The reduction of the zinc ores was formerly carried on in England by a process termed distillation *per descensum* The mixture of ore and coal was heated in crucibles closed at the top, but having a pipe leading from the bottom stopped by a wooden plug. The latter was quickly carbonised, thus becoming porous and allowing the vapour of the reduced zinc to pass down the tube, where it was condensed. This plan necessitated a large consumption of fuel, and has therefore been abandoned.

In the Belgian process, tube-shaped retorts made of refractory fire-clay are employed. These may be either circular or elliptical in cross-section, and vary from 3 feet 3 inches to 5 feet in length, the circular retorts being about 6 to 10 inches in diameter, and the elliptical retorts about 7 inches by 9 inches. To the open end a conical clay tube is luted, about 16 inches in length, and having a diameter of 6 inches at one end and 3 inches at the other, and to this adapter is fitted a sheet-iron condenser or nozzle which serves to catch any particles of metal, and to condense zinc fume. The furnaces in which these retorts are heated were formerly fired with coal, but now gas-fired furnaces are often used with or without

[1] *Zeit. Ver. Deutsch. Ing.*, 1872, 505.

Siemens' regenerator arrangement. Fig. 165 shows such a furnace with regenerators.

The number of retorts per furnace varies considerably. In coal-fired furnaces from 6 to 9 rows are used, and each furnace may have 48 or more retorts. In gas-fired furnaces 4 to 6 rows only are used, but these are much longer and may have from 56 to 72 retorts in each row. The retorts are fixed in a slightly slanting direction to allow the spent charge to be easily withdrawn at the end of the operation.

A mixture of 2 parts of ground roasted ore and 1 part of coal dust is brought into the retorts, each holding about 40 lbs.

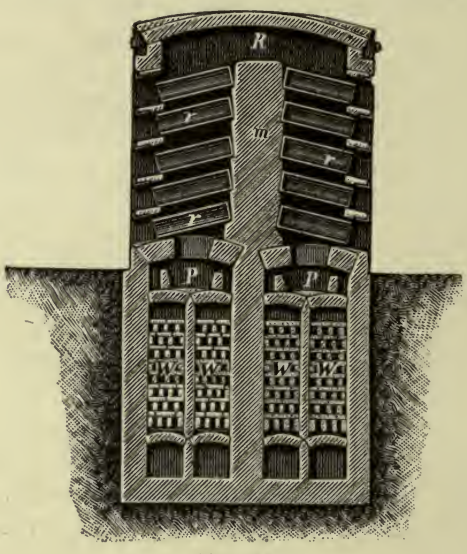


Fig. 165.

of the mixture. As soon as the temperature has risen high enough, the reduction begins, and carbon monoxide is evolved and burns from the end of the clay adapter with a blue flame. After a while the flame becomes much more brilliant, showing that the metal is beginning to volatilise; the iron condenser is then placed on to the end of the clay adapter, and the metallic vapours are thus condensed. After about three hours the iron condenser is taken away and the oxide knocked out. A ladle is then held under the mouth of the clay adapter, and the melted zinc which has accumulated therein is scraped out. The iron receiver is then again fixed in its place, and after a further period of four hours the operation is repeated. It is

completed in about twenty hours. The exhausted charge is then removed from the retort and a fresh one introduced. In this way one charge is worked off from each retort in twenty-four hours.

In the *Silesian process*, clay retorts or muffles (Fig. 166) about 1 metre long are arranged side by side in the horizontal bed of a reverberatory furnace (Fig. 167). No fewer than 30 or 40 muffles are thus arranged, and these may contain 1,500 to 2,000

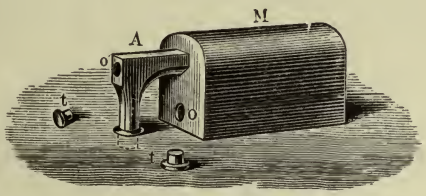


Fig. 166.

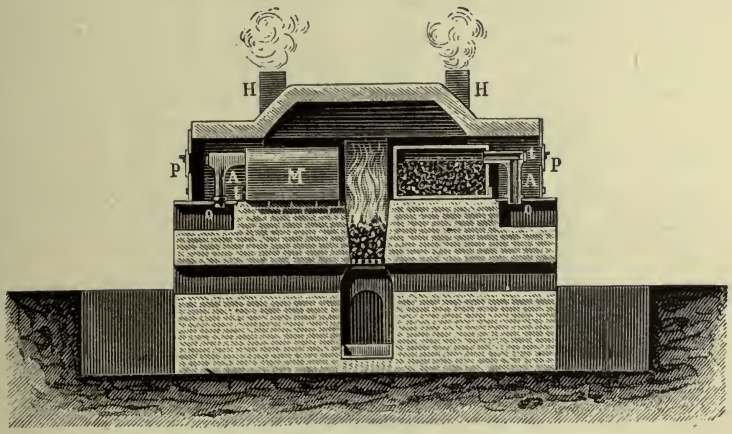


Fig. 167.

kilos. of the mixture of coal and roasted ore. This mixture is introduced through a luted clay door in the muffle or retort. When the temperature has risen sufficiently high, the vapour of the reduced zinc passes out of the retort by a bent clay pipe (A, Fig. 166), and condenses in an iron tube, falling down into an iron tray placed in a closed recess (O, Fig. 167), in the furnace. In this process a considerable quantity of zinc is burnt, producing zinc oxide, known as Silesian zinc-flowers.

A combination of the Belgian and Silesian methods is being largely employed in the Belgo-Silesian furnace (Fig. 168). One modification of this consists of a furnace, having three rows of

muffles, the bottom row being supported throughout their whole length upon the hearth, while the upper rows are supported at their ends only, as in Belgian furnaces. These furnaces are generally gas-fired, arrangements being made for heating the air necessary for the combustion by means of the heat of the waste gases.

Other methods for extracting zinc from its ores have been used with more or less success; these include reduction in electric furnaces of the "arc" and also of the "resistance" type, and also wet processes in which the zinc is first brought into

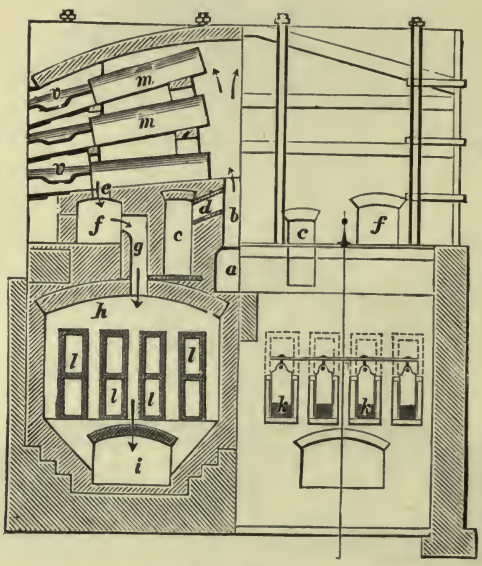


Fig. 168.

solution, and then either precipitated as a compound suitable for reduction or as metallic zinc by electro-deposition.

Commercial zinc is seldom perfectly pure. It almost always contains small quantities of lead, iron, and carbon. Not infrequently silver, cadmium, and small traces of arsenic, antimony, and other metals are met with. The chemical purity of zinc may be readily ascertained by the fact that, when pure, it is scarcely attacked by dilute sulphuric acid, whereas common impure zinc dissolves readily under the same circumstances (p. 649).

296 *Properties.*—Zinc has a bluish-white colour, melts at a temperature of 419° (Heycock and Neville), and boils at 918°

(D. Berthelot).[1] The vapour density of zinc is 2·36, so that its molecular and atomic weights are identical.[2] If zinc is heated to its melting point, but not to a higher temperature, poured out upon a non-conducting surface, and the molten metal then poured off from the portion which has solidified, the metal is obtained in the crystalline form, consisting of hexagonal prisms and pyramids or rhombohedra. Commercial zinc has a coarsely laminar texture. It is moderately hard and difficult to file, and when bent after fusion emits a crackling noise, not so loud as that emitted by tin. Zinc exhibits the greatest degree of ductility and malleability at temperatures between 100° and 150°, at which it may be drawn out into wire and rolled into plate.[3] On the other hand, it is so brittle at 205° that it may be powdered in a mortar. The specific gravity of zinc which has been distilled in vacuo is 6·9225 at 20°/4°, and this rises to 7·1272 when the metal is submitted to a pressure of 10,000 atmospheres.[4]

Zinc has been obtained by the electrical method in the colloidal state, forming a brown solution in ether,[5] and also as an unstable hydrosol.[6]

Zinc vapour readily burns in air, the combustion being shown by holding thin zinc turnings in the flame of a lamp, or better still, by placing zinc in a white-hot crucible, and exposing the surface to the air or stirring it with an iron rod, when the metal burns with a bright white flame.

Pure zinc is very slowly dissolved by dilute sulphuric acid, whilst the impure metal readily dissolves with evolution of hydrogen. The inactivity of the former is due to the fact that a film of hydrogen forms on the surface of the zinc and prevents the further action of the acid; if, however, impurities are present, these form galvanic couples with the zinc, and as they are electro-negative to zinc the hydrogen is evolved from them, leaving the surface of the zinc continuously exposed to the action of the acid.[7] If a few drops of a solution of the sulphate of

[1] *Compt. rend.*, 1900, **131**, 380; 1902, **134**, 705. Compare Le Chatelier, *ibid.*, 1895, **121**, 323.

[2] V. Meyer, *Ber.*, 1886, **19**, 3295. See also Biltz, *Journ. Chem. Soc.*, 1896, **70**, ii, 152.

[3] Hobson and Sylvestra, *Gilbert's Ann.*, 1806, **24**, 104.

[4] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.

[5] Svedberg, *Ber.*, 1905, **38**, 3616.

[6] Billitzer, *Ber.*, 1901, **35**, 1929.

[7] Weeren, *Ber.*, 1891, **24**, 1785.

copper, cobalt, or nickel,[1] or of platinum chloride, be added to the acid in which the pure zinc is placed, hydrogen is rapidly evolved, owing to the deposition of copper or platinum on the zinc, which acts in the manner above described. When zinc is heated with concentrated sulphuric acid, sulphur dioxide is evolved, and no hydrogen sulphide is produced.[2] Zinc dissolves also in hydrochloric acid with evolution of hydrogen and formation of the chloride; with nitric acid, solution also takes place, with evolution of nitric oxide, nitrous oxide, or ammonia according to the conditions of the experiment, the last named uniting with the excess of nitric acid to form ammonium nitrate. Zinc dissolves also in solutions of the alkalis with evolution of hydrogen, the zinc hydroxide first formed dissolving in the excess of alkali.

Zinc when exposed to the atmosphere is gradually attacked, a scale of basic carbonate being formed,[3] and it is also attacked and partially dissolved by water.[4]

Commercial zinc usually contains arsenic, which may be removed by adding 0·2 per cent. of metallic sodium to the fused metal, skimming off the surface layer and then granulating the metal by pouring it into cold water.[5]

Zinc is largely employed in the form of sheets for a variety of technical purposes, and is also much used in the manufacture of brass, an alloy of the metal with copper. Zinc is also used for desilverising lead, for galvanising iron, for electrical batteries, for the precipitation of gold from its solution in potassium cyanide, and for a great number of other purposes. Metallic zinc in the form of fine dust is obtained in considerable quantity in the manufacture of the metal, mixed with a certain amount of oxide of zinc. This mixture, called *zinc dust*, is a valuable reducing agent, often used for this purpose in organic chemistry, and also on a large scale for the reduction of indigo-blue: it is likewise employed as a paint for iron articles. In order to free the powder from oxide of zinc, it is only necessary to allow it to remain for some time in contact with very dilute hydrochloric acid. The residue is first washed with

[1] See Ball, *Journ. Chem. Soc.*, 1897, **71**, 642.

[2] Berthelot, *Ann. Chim. Phys.*, 1898, [7], **14**, 176; Adie, *Proc. Chem. Soc.*, 1899, **15**, 133.

[3] Moody, *Proc. Chem. Soc.*, 1903, **19**, 273.

[4] Davies, *J. Soc. Chem. Ind.*, 1899, **18**, 102.

[5] Hehner, *J. Soc. Chem. Ind.*, 1902, **21**, 675; Thorne and Jeffers, *Analyst*, 1906, **31**, 101.

water and then with pure alcohol, after which it is dried and preserved. If exposed to the air in mass in a damp state, it is liable to ignite spontaneously.

Alloys of Zinc.

297 The most important alloys of zinc are those which it forms with copper, which, as already stated, were known long before metallic zinc had itself been isolated.

The following table gives the composition of a variety of copper-zinc alloys:—

	Gold-like alloy used by watch-makers.	Aich's metal	Brass from			Tombac.		Roman coin of the reign of Titus.
			Ocker.	Stöll-berg.	Eng-land.	English.	Viennese.	
Copper ..	58·86	60·20	62·24	65·80	70·30	86·38	97·8	96·06
Zinc	40·22	38·10	37·27	33·80	29·30	13·61	2·2	2·71
Tin	—	—	0·12	0·25	0·17	—	—	—
Lead	1·90	—	0·59	0·28	0·28	—	—	—
Iron	—	1·60	0·12	—	—	—	—	0·85
	100·98	99·90	100·34	100·13	100·05	99·99	100·0	99·62

Brass, which has long been known, was up to the year 1780 always made by strongly heating copper together with calamine and charcoal or coal. The coal reduces the calamine to the metallic condition, and the zinc, instead of passing off as vapour, combines with the copper, and forms brass. At the present day, however, brass is prepared by adding the requisite quantity of metallic zinc to molten copper. The composition of brass varies considerably; common brass, sometimes termed English brass, contains about two parts of copper to one of zinc. When more copper is added the colour becomes reddish. That containing about 80 per cent. of copper is termed German or Dutch brass or tombac. On the other hand, an additional proportion of zinc yields a light yellow metal known as Muntz metal, an alloy which was first prepared by Muntz, in the year 1832, and has since been very largely used for the sheathing of ships. Another such alloy, named Aich's metal from its inventor, is malleable when hot.

Brass and the other copper-zinc alloys are all harder than

copper; they are malleable, and can be hammered and rolled into thin plates and drawn out to fine wire; they can also be readily worked in the lathe. These properties, as well as their beautiful colour, bright lustre, and cheapness, render them most useful in the arts and manufactures.

COMPOUNDS OF ZINC.

Zinc and Oxygen.

298 *Zinc Oxide*, ZnO.—This compound occurs as the mineral zincite or red zinc ore, which consists of a mixture of zinc oxide with 0·7 to 12 per cent. of red oxide of manganese. It occurs, especially in New Jersey, in red or orange-yellow hexagonal crystals or in a granular mass. Zinc oxide is also occasionally found in the crystalline state in brass-melting furnaces, as well as in the zinc furnaces. It has already been mentioned that the finely divided oxide was known to the ancients as tutia, pompholyx or flowers of zinc, and Dioscorides states that if too much cadmia is employed in the manufacture of brass, pompholyx is formed like tufts of wool,[1] whence the name *Lana philosophica* was given to this substance by the alchemists. The similarity between the oxide of zinc obtained by combustion and flakes of snow led the alchemists to term it *nix alba*; this was translated into German as "weisses Nichts," and retranslated into Latin as "nihilum album."

Zinc oxide is known in commerce as "zinc white," and is prepared on the large scale and used as a paint. It is obtained by the distillation of zinc in earthenware retorts, the burning vapours of the zinc being brought into chambers through which a current of air is passed and the oxide allowed to deposit in a second chamber. The preparation of zinc white directly from the ore has been carried on at Liége.[2]

Zinc oxide is prepared for pharmaceutical purposes by precipitating a solution of zinc sulphate with sodium carbonate and igniting the basic carbonate thus thrown down. As the commercial zinc sulphate frequently contains Epsom salts (magnesium sulphate) as an impurity, it is best, in order to obtain the pure compound, to dissolve zinc in dilute sulphuric acid,

[1] πομφόλυξ ἐρίῳ τολύπαις ἀφομοιοῦται.

[2] See Hofmann's *Ber. Entw. Chem. Ind.*, i., 919.

and then either to treat the solution with sulphuretted hydrogen, or to allow the solution to remain for some time in contact with metallic zinc, in order to precipitate the cadmium, copper, arsenic, and other metals. To the filtrate a small quantity of an alkaline solution of sodium hypochlorite is added, in order to throw down the iron, manganese, &c.; the solution is then filtered, and poured in a thin stream into a boiling solution of pure sodium carbonate. The precipitate is washed with boiling water, and, after drying, it is gently ignited in a glass flask or platinum basin.

Zinc oxide has a specific gravity of 5·6; when hot it possesses a lemon-yellow colour, but on cooling it becomes white.[1] When heated in the oxy-hydrogen flame it emits a brilliant white light, and after being thus heated, phosphoresces for some time in the dark. It evaporates at an appreciable rate at 1400° and rapidly volatilises in the electric furnace, the vapour condensing in long, transparent crystals.[2] It is probable that the oxide undergoes polymerisation when heated, a small amount of heat being evolved in the process. The anhydrous oxide gradually takes up water from the air.[3]

The reduction of zinc oxide by carbon in an atmosphere of nitrogen begins at 800°, and increases rapidly with rise of temperature. Its reduction by carbon monoxide begins at 600°, and also increases rapidly with rise of temperature.[4]

It readily dissolves in acids, forming the corresponding zinc salts, which are colourless, unless the acid be coloured. The normal soluble salts redden litmus solution; they possess a disagreeable metallic taste, and act as poisons and emetics.

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white powder, when caustic potash, caustic soda, or ammonia is added to a solution of a zinc salt, but when prepared in this way it usually contains small amounts of a basic zinc salt. It is very soluble in an excess of these reagents, zinc oxide acting as an acid-forming oxide towards the strong alkalis, and it is upon this fact that the solution of zinc in alkalis with evolution of hydrogen depends. This reaction takes place especially quickly in presence of metallic iron. If metallic zinc is allowed to

[1] Compare Schüpphaus, *J. Soc. Chem. Ind.*, 1899, **18**, 987.

[2] Moissan, *Compt. rend.*, 1892, **115**, 1034.

[3] de Forcrand, *Compt. rend.*, 1902, **134**, 1426; **135**, 36; *Ann. Chim. Phys.*, 1902, [7], **27**, 26.

[4] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 290.

remain under the surface of a solution of ammonia in contact with iron or copper, zinc hydroxide crystallises from the solution in colourless, transparent rhombic prisms (Runge); and if a saturated solution of the hydroxide in caustic potash is allowed to stand, regular octahedra of the compound, $Zn(OH)_2,H_2O$, are formed (Bödeker).

The crystalline hydroxide is stable up to 85° in the air, but loses all its water at 130–140°, except a trace which is driven off only at a red heat. The amorphous hydroxide, on the other hand, loses its water gradually as the temperature rises (de Forcrand). The hydroxide is soluble in about 190,000 parts of water at 18°.[1] It is readily soluble in caustic alkalis and in ammonia, but is insoluble in dimethylamine.[2]

In its behaviour to alkalis it may be regarded as a weak acid, H_2ZnO_2, but the salt formed is very largely hydrolysed, the amount of the hydroxide dissolved by an alkali being a function of the concentration of the latter.[3] Freshly precipitated zinc hydroxide requires nearly 7 molecular proportions of caustic soda in concentrated solution to dissolve it completely, and the solution thus formed is not permanent, zinc hydroxide being gradually precipitated from it in a less soluble form. Only a very small amount of a sodium zincate is ever present in the solution, the greater part of the dissolved hydroxide being probably present in the colloidal state.[4] When the hydroxide dissolves in ammonia, on the other hand, a complex hydroxide, the formula of which is still unsettled, is probably formed.[5]

Zinc Peroxide, ZnO_2.—A product containing zinc peroxide is formed by the action of hydrogen peroxide on the hydroxide,[6] and by the electrolysis of a solution of zinc chloride with a porous diaphragm, hydrogen peroxide being added to the cathode compartment.[7] It forms a yellowish powder containing variable amounts of zinc hydroxide and water.[8] Zinc peroxide

[1] Dupré, jun., and Bialas, *Zeit. angew. Chem.*, 1903, **16**, 54.

[2] Herz, *Zeit. anorg. Chem.*, 1901, **26**, 90.

[3] Rubenbauer, *Zeit. anorg. Chem.*, 1902, **30**, 331; Moir, *Proc. Chem. Soc.*, 1905, **21**, 310. See also Kuriloff, *Zeit. Elektrochem.*, 1906, **12**, 209; *Bull. Acad. St. Pétersbourg*, 1901, **1**, 95.

[4] Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 289.

[5] Dawson and McCrae, *Journ. Chem. Soc.*, 1900, **77**, 1239; Euler, *Ber.*, 1903, **36**, 3400; Bonsdorff, *Zeit. anorg, Chem.*, 1904, **41**, 132.

[6] Kuriloff, *Compt. rend.*, 1903, **137**, 618; de Forcrand, *ibid.*, 1902, **134**, 601; **135**, 103.

[7] Foregger and Philipp, *J. Soc. Chem. Ind.*, 1906, **25**, 398.

[8] Hinz, German Patent, 151129.

may also be formed by the action of 30 per cent. hydrogen peroxide solution on potassium, sodium, or ammonium zinc-oxide.[1]

Zinc and the Halogens.

299 *Zinc Chloride*, $ZnCl_2$.—Impure chloride of zinc was first prepared by Glauber. He describes in his *De furnis novis philosophicis*, published in 1648, an *oleum lapidis calaminaris*, "obtained by dissolving calamine in spirit of salt, and heating the solution, when a thick *oleum* remains as unctuous as olive-oil, and not particularly corrosive, for the spirit of salt has itself been weakened by corroding the calamine and thus lost its acrimony. This oil must be well preserved against the action of the air, otherwise in a few days it attracts so much air to it that it becomes a watery liquid." In 1735 Hellot prepared "butter of zinc," by distilling flowers of zinc with sal-ammoniac; and Pott, in 1741, obtained the same substance by distilling zinc with corrosive sublimate. Gallisch, in 1782, noticed that zinc deliquesced when exposed to the action of dephlogisticated muriatic acid gas (chlorine), and Westrumb, in 1790, observed that when finely divided zinc was dropped into the gas, the metal took fire. This historical sketch serves to show the methods by which the anhydrous chloride may be obtained. The same substance is formed when a mixture of anhydrous zinc sulphate and calcium chloride is distilled (Persoz).

Zinc chloride is a white or usually greyish-white mass of sp. gr. 2·907 at 25°/4°, soft, like wax, at the ordinary temperature, melting when heated a little above 100° (H. Davy), and subliming at a higher temperature in white, needle-shaped crystals. It is very deliquescent, is soluble in alcohol, and boils at 730°, its vapour density being 4·6, corresponding to the normal formula. It also has the normal molecular weight when dissolved in urethane, as determined by the freezing point method (Castoro).[2]

A concentrated solution of zinc chloride is best obtained by dissolving zinc, its oxide, or carbonate, in hydrochloric acid, and

[1] Kazanecky, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1452; see also Carrasco, *Gazz.*, 1911, **41**, i., 16; and Teletoff, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 131.

[2] *Gazz.*, 1898, **28**, ii., 317.

evaporating the solution to the consistency of a syrup. On the addition of a little concentrated hydrochloric acid to this syrupy solution, small deliquescent octahedra separate out, having the composition $ZnCl_2,H_2O$. In addition to this, hydrates with 1·5, 2·5, 3, and $4H_2O$ are known, the curve of equilibrium for zinc chloride and water being one of great complexity.[1] Zinc chloride is used in surgery as a caustic, and is employed in the laboratory for the purpose of separating the elements of water from many organic substances. It is also employed on a large scale, as is magnesium chloride, for weighting cotton goods. When its solution is evaporated, hydrochloric acid is evolved and basic salts are formed; these may also be obtained by diluting the aqueous solution, and by boiling the solution of the chloride with zinc oxide and adding water, when precipitates are formed consisting of mixtures of Zn(OH)Cl and $Zn(OH)_2$ in varying proportions. The oxychlorides, $ZnCl_2,4ZnO,6H_2O$ and $2ZnCl_2,2ZnO,3H_2O$, have been described by Driot.[2] When a solution having a specific gravity of 1·7 is boiled with an excess of oxide, a liquid is formed which has the property of dissolving silk, and this is used for separating silk fibres from those of wool, or of cotton or linen, whilst all of these dissolve in a solution of normal zinc chloride.

Zinc chloride forms double salts with 2 and 3 molecules of ammonium chloride;[3] the products obtained by the crystallisation of solutions containing chloride of zinc and the chlorides of sodium, potassium, ammonium, and lithium at temperatures between 20° and 100° have been examined by Ephraim.[4]

Zinc Bromide, $ZnBr_2$, is formed when bromine vapour is passed over the metal heated to redness. It corresponds closely to the chloride in its properties, and on heating sublimes in the form of white needles. It melts at 394°, and boils at 650°. The products of crystallisation of solutions containing bromide of zinc and the bromides of sodium, potassium, ammonium, and lithium at temperatures between 20° and 100° have been examined by Ephraim.[5]

Zinc Iodide, ZnI_2.—Zinc and iodine readily unite when they

[1] Dietz, *Ber.*, 1899, **32**, 90; Mylius and Dietz, *ibid.*, 1905, **38**, 921.

[2] *Compt. rend.*, 1910, **150**, 1426.

[3] Meerburg, *Zeit. anorg. Chem.*, 1903, **37**, 199.

[4] *Zeit. anorg. Chem.*, 1908, **59**, 56; see also Ephraim and Model, *ibid.*, 1910, **67**, 379.

[5] *Zeit. anorg. Chem.*, *loc. cit.*

are heated together to form a colourless mass which melts at 446°, and sublimes in four-sided needles. An aqueous solution can be easily obtained by warming metallic zinc and iodine together with water. On evaporating the solution, the anhydrous compound separates out in the form of regular octahedra, which when exposed to the air first absorb water and deliquesce, and then take up oxygen and lose iodine.

Zinc and Sulphur.

300 *Zinc Sulphide*, ZnS, is found as *blende*, which crystallises in the regular system, frequently in hemihedral forms (Class 31, p. 201). Its specific gravity varies from 3·5 to 4·2. In the pure state it is transparent, and has a light yellow colour; usually, however, it contains iron and other metals which impart to it a red, brown, or black tint. The same compound is more rarely found as wurtzite in hexagonal crystals. When ammonium sulphide is added to a solution of a zinc salt, a white amorphous precipitate of zinc sulphide is formed; this is soluble in dilute acids, with the exception of acetic acid, with evolution of hydrogen sulphide. When this precipitate is heated in a current of hydrogen, or when zinc oxide is ignited in an atmosphere of sulphuretted hydrogen, zinc sulphide is obtained in crystals which have the form of wurtzite. Natural crystals of zinc sulphide have the property of phosphorescing after exposure to light, and the phosphorescent sulphide may be artificially prepared by heating precipitated zinc sulphide to whiteness in a covered crucible (Sidot). Pure zinc sulphide remains non-phosphorescent, but if the material contains small amounts of alkali chlorides and the sulphides of other metals, such as bismuth, copper, or manganese, a brilliant phosphorescence is obtainable.[1] The phosphorescent sulphide glows when exposed to X-rays, Becquerel rays, or the α-radiation from radium, and when placed in ozonised oxygen.[2] For the action of the Röntgen rays on a crystal of zinc sulphide see p. 207.

Zinc Sulphate, $ZnSO_4$.—This salt, long known under the name of white vitriol, is thus described in the first book of "Basil Valentine's" *Last Testament*—"Behold the ▽ (water) of Goslar, how a fine white and red vitriol is found there." The

[1] Grüne, *Ber.*, 1904, **37**, 3076; Hofmann and Ducca, *ibid.*, 3407; Jorissen and Ringer, *Chem. Centr.*, 1906, **1**, 644.

[2] Schenck and Mihr, *Ber.*, 1904, **37**, 3464.

name vitriol was applied to all the salts of the common metals possessing a vitreous lustre,[1] and to this day iron sulphate is known as green vitriol, and copper sulphate as blue vitriol.

White vitriol was prepared on the large scale at Goslar, in the Harz, in the sixteenth century. It was obtained by lixiviating the roasted ore, but its composition remained long unknown. Thus, in Lemery's *Cours de Chymie*, published in 1675, we read, "Le vitriol blanc est le plus dépuré de substance metallique." It was, indeed, soon discovered that this salt might be obtained by dissolving calamine in sulphuric acid, but as this ore always contains iron, green vitriol was obtained at the same time. In addition to this, the fact that both green vitriol and blue vitriol when heated become white through loss of water of crystallisation led to still further confusion between these compounds. It was not until 1735 that Neumann suggested that the base of white vitriol consisted of zinc or calamine, and this view was confirmed by Hellot, inasmuch as he obtained the salt by dissolving zinc in dilute sulphuric acid, whilst Brandt showed that brass was obtained from white vitriol by calcining it and heating it with charcoal and copper.

Zinc sulphate occurs not unfrequently in zinc mines, where it is formed by the oxidation of blende. It is, however, usually obtained on the large scale by roasting ores containing sulphide of zinc, afterwards exhausting with water, and evaporating the solution to the crystallising point, when the hydrate $ZnSO_4,7H_2O$, isomorphous with Epsom salts, separates out. These crystals on heating fuse readily in their water of crystallisation. Commercial zinc vitriol is made to assume the shape of a sugar-loaf by stirring this fused mass in wooden troughs with wooden shovels till crystallisation takes place, and subsequently pressing the mass into moulds. The aqueous solution has an acid reaction (p. 102), 0·03 per cent. of the salt being hydrolysed in a 1/16 normal solution.[2]

Zinc sulphate forms several hydrates. The heptahydrate is stable in contact with water up to 39°, and then passes into the

[1] "Atramentum candidum potissimum stiriæ figura reperitur Goslariæ, translucidum cristalli instar; nec cæruleum nec viride caret perspicuitate; unde superior ætas atramento sutorio vitrioli nomen imposuit."—Agricola, *De Natura Fossilium*, Lib. III. ed. 1657.

[2] Ley, *Ber.*, 1897, **30**, 2192.

hexahydrate, which at 70° is converted into a lower hydrate probably the monohydrate.[1]

One hundred parts of water dissolve :

	At 0°	15°	39°	50°	70°	100°
$ZnSO_4$	41·9	50·88	70·06	76·84	89	78·5.

The heptahydrate has the specific gravity 1·95 : it effloresces slowly in the air, and on heating to 100° loses six molecules of water, the last molecule being evolved only at a moderate red-heat. The hexahydrate, isomorphous with the corresponding magnesium salt, separates out when a solution of the sulphate is evaporated above 50°.

The anhydrous salt forms a friable mass having a specific gravity of 3·4. When heated more strongly, sulphur dioxide and oxygen are evolved, and a basic salt remains behind, which is formed also when zinc sulphate and zinc oxide are boiled together. On cooling the hot saturated solution, glistening scales separate out having the formula $SO_2(O{\cdot}Zn{\cdot}O{\cdot}Zn)_2O,2H_2O$. At a white heat all the zinc sulphates are completely decomposed, leaving a residue of zinc oxide. Besides these, several other basic zinc sulphates are known, and also characteristic double salts with the alkali sulphates, having the general formula $ZnSO_4,M_2SO_4,6H_2O$.[2]

Zinc sulphate is employed in medicine, in dyeing, and in the manufacture of lithophone.

Zinc Thiosulphate, ZnS_2O_3, is prepared by treating a mixture of zinc dust and water at 45–50° with a rapid stream of sulphur dioxide until the metal has entirely dissolved ; a large excess of sulphur dioxide must be avoided, as this reacts with zinc thiosulphate, forming polythionic acids. The viscid, greyish-yellow mass produced, when cooled to the ordinary temperature, sets to a stiff paste which is drained in an inert atmosphere.[3]

Zinc and Nitrogen and Phosphorus.

301 *Zinc Nitride*, Zn_3N_2, is formed when zincamide is heated to dull redness :

$$3Zn(NH_2)_2 = Zn_3N_2 + 4NH_3,$$

[1] See Landolt-Börnstein-Roth, *Physikalisch-chemische Tabellen*, 1912, 499.

[2] Tutton, *Journ. Chem. Soc.*, 1904, **85**, 1123 ; Koppel, *Zeit. physikal. Chem.*, 1905, **52**, 385. See also Mallet, *Journ. Chem. Soc.*, 1900, **77**, 220.

[3] Gränau, Landshoff and Meyer, D. R. Patent, 184564.

and is also produced to some extent when zinc is heated at 600° in a current of ammonia.[1] It is a green powder which is decomposed by water with such energy that the mass when moistened becomes incandescent:

$$Zn_3N_2 + 3H_2O = 3ZnO + 2NH_3.$$

Zincamide or *Zinc Diamine*, $Zn(NH_2)_2$, is formed by the action of dry ammonia on zinc ethyl:

$$Zn(C_2H_5)_2 + 2NH_3 = Zn(NH_2)_2 + 2C_2H_6.$$

It is a white, amorphous powder and is decomposed by water with evolution of heat as follows:

$$Zn(NH_2)_2 + 2H_2O = Zn(OH)_2 + 2NH_3.$$

Zinc Hydrazide, ZnN_2H_2, is formed by the interaction of zinc ethyl, dissolved in dry ether, and hydrazine. It may also be prepared from zincamide and anhydrous hydrazine in ethereal suspension.[2]

Zinc Nitrate, $Zn(NO_3)_2$.—The hexahydrate crystallises from a very concentrated solution of zinc in nitric acid, in striated colourless pointed four-sided prisms. These are very deliquescent, and are soluble in alcohol. It melts at 36·4°, and passes at about 35°, and at a concentration of 65 per cent. of anhydrous salt, into the trihydrate, which melts at 45·5°. A hydrate with $9H_2O$ also exists below −17°.[3] When heated for some time at 100°, the salt loses water and nitric acid and a basic nitrate remains, which is also formed by boiling the solution with zinc oxide. Hydrates with 2, 4, and 6 molecules of water are also known, and the interactions between these have been investigated by Vasilieff.[4]

Zinc Phosphide, Zn_3P_2, is obtained as a grey mass by heating finely divided zinc in the vapour of phosphorus (Schrötter).[5] Zinc phosphide is employed in medicine.

Zinc and Carbon.

302 *Carbonates of Zinc.—Normal Zinc Carbonate*, $ZnCO_3$ occurs as zinc-spar or calamine, crystallising in rhombohedra

[1] White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343.
[2] Ebler and Krause, *Ber.*, 1910, **43**, 1690.
[3] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 400.
[4] *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 748.
[5] See also Vigier, *Bull. Soc. chim.*, 1861, **3**, 5, and Jolibois, *Compt. rend.*, 1908, **147**, 801.

having a specific gravity of 4·42. Zinc-spar is found sometimes in the pure state, but, in general, more or less of the zinc is found to be replaced by magnesium, cadmium, iron, and other isomorphous metals. When a solution of zinc vitriol is precipitated by the addition of an alkali carbonate or bicarbonate, the first product is the amorphous normal carbonate, which passes into the hydrated crystalline carbonate, $ZnCO_3,H_2O$, or into the basic carbonate, $5ZnO,2CO_2,4H_2O$, or into a mixture of these, according to the concentration of the solutions and the temperature. The basic carbonate may be obtained pure by dissolving zinc carbonate or oxide or metallic zinc in water containing carbon dioxide and boiling the solution. When boiled with an excess of sodium carbonate it is finally converted into anhydrous zinc oxide.[1]

Zinc Cyanide, $Zn(CN)_2$, is a snow-white powder used in medicine, and prepared by precipitating zinc acetate with aqueous hydrocyanic acid. It is insoluble in water and in alcohol, but dissolves in solutions of cyanide of ammonium and potassium, forming double salts [2] such as $K_2Zn(CN)_4$.

Ammoniacal Derivatives of Zinc.

303 These compounds closely resemble the corresponding derivatives of the cupric salts (p. 441). *Zincammonium chloride*, $ZnCl_2,4NH_3,H_2O$, is obtained by adding ammonia to a solution of zinc chloride until the precipitate first formed redissolves, and on the evaporation of the solution crystallises out in nacreous plates. When heated to 149° it is converted into $ZnCl_2,2NH_3$, which crystallises in rhombic prisms, and on further heating loses ammonia, forming the compound $ZnCl_2,NH_3$; the latter is an amber-coloured mass which distils at a red-heat without decomposition.[3]

Zinc sulphate also yields crystalline ammonia derivatives, having the composition : $ZnSO_4,2NH_3,H_2O$; $ZnSO_4,4NH_3,4H_2O$. The anhydrous sulphate also combines directly with ammonia, forming the compound $ZnSO_4,5NH_3$, which is a white powder and is decomposed by water with separation of zinc hydroxide.

When zinc sulphate solution is treated with excess of ammonia, the clear solution probably contains the complex salt $Zn(NH_3)_4SO_4$ (Dawson and McCrae).

[1] Kraut, *Zeit. anorg. Chem.*, 1896, **13**, 1.
[2] Sharwood, *J. Amer. Chem. Soc.*, 1903, **25**, 570.
[3] Kane, *Ann. Chim. Phys.*, 1839, **72**, 290.

Detection and Estimation of Zinc.

304 The salts of zinc do not, as a rule, impart any tint to the non-luminous gas-flame, but a few of the salts formed from volatile acids, such as the nitrate, produce a green coloration. The spark spectrum of zinc, however, is characteristic, and can be well shown by volatilising a small piece of the metal in the lower carbon pole of the electric lamp. Amongst the more prominent zinc lines are 6363 and 6102 in the red, and 4926 and 4911 in the blue.

The most characteristic compound of zinc is the white sulphide insoluble in water, in acetic acid, and in the alkalis. In the ordinary course of qualitative analysis zinc is thrown down together with the other metals precipitated by ammonium sulphide, such as cobalt, nickel, iron, manganese, chromium, and aluminium, the first four being precipitated as sulphides, the last two as hydroxides. The well-washed precipitate is treated with dilute hydrochloric acid, which leaves nickel and cobalt sulphides undissolved; the filtrate is boiled and a little potassium chlorate is added to remove sulphuretted hydrogen and oxidise the iron to the ferric state; ammonia is then added, which precipitates the iron, chromium, and aluminium, as hydroxides. The filtrate is acidified, mixed with an excess of sodium acetate, and sulphuretted hydrogen passed through the solution; zinc is thus precipitated as the sulphide, manganese remaining in solution. When a zinc compound is ignited on charcoal before the blowpipe, and the heated mass is moistened with a solution of cobalt nitrate and again ignited, a beautiful green mass, known as Rinmann's green, is obtained. Zinc compounds heated in the blowpipe flame on charcoal with sodium carbonate yield an incrustation of zinc oxide, which when hot is yellow, but on cooling becomes white.

Small traces of zinc can be readily and accurately detected by *Bunsen's method of flame-reactions*. This depends upon the fact that the more volatile metals, such as zinc, mercury, and arsenic, are reduced from their compounds when these are heated on a thread of asbestos held in the upper reducing flame of the Bunsen burner. If a small porcelain basin, filled with cold water, be held just above the substance to be examined, the volatilised metal condenses on the outside of the cold basin as a metallic film, and in a few seconds the reaction is complete. A square

centimetre of filter paper is moistened with nitric acid, and this rubbed over the surface of the basin so as to dissolve the metallic film; the paper is then rolled up, placed in a coil of thin platinum wire, and burned in the upper oxidising flame at as low a temperature as possible, when the colour of the ash is seen to be yellow when hot, but white on cooling. The ash is next moistened with a drop of dilute cobalt solution, and heated in the flame, when the mass attains a green colour.

For the quantitative estimation of zinc, the solution is precipitated with a boiling solution of sodium carbonate, the basic carbonate washed and dried and converted by ignition into zinc oxide, which is then weighed. Zinc may also be estimated gravimetrically by the electrolysis of an alkaline solution of the hydroxide, and volumetrically by titration with a standardised solution of sodium sulphide or potassium ferrocyanide, a solution of ammonium molybdate or uranium acetate being used as indicator when ferrocyanide is employed.

Atomic Weight of Zinc.—This was determined by Marignac[1] from the quantity of zinc and chlorine contained in potassium zinc chloride, K_2ZnCl_4, his results giving an average value of 65·25, whilst Baubigny[2] by analysis of the sulphate obtained the number 65·40. Morse and Burton,[3] from the amount of zinc oxide yielded by pure zinc, the metal being converted into the nitrate and this decomposed by heating, arrived at the number 65·26; they, however, neglected the amount of oxygen and nitrogen occluded by zinc oxide under these circumstances, and a repetition[4] of their experiments, in which allowance was made for this source of error, led to the number 65·45. Gladstone and Hibbert[5] found the ratio of the equivalents of zinc and silver as determined by comparing the quantity of zinc dissolved and silver precipitated by the same current to be 3·298, from which, taking silver as 107·88, the atomic weight of zinc is found to be 65·41. Finally, Richards and Rogers,[6] by the analysis of zinc bromide prepared from pure zinc oxide or electrolytic zinc, found the atomic weight to be 65·38. The value which is at present (1913) accepted is 65·37.

[1] *Jahresb.*, 1883, 42. [2] *Compt. rend.*, 1883, **97**, 908.
[3] *Amer. Chem. J.*, 1888, **10**, 311.
[4] Morse and Arbuckle, *Amer. Chem. J.*, 1898, **20**, 195.
[5] *Journ. Chem. Soc.*, 1889, **55**, 443. [6] *Zeit. anorg. Chem.*, 1895, **10**, 1.

CADMIUM. Cd = 112·40.

305 This metal was discovered in the year 1817 by Stromeyer. He observed that a sample of zinc carbonate obtained from the zinc works at Salzgitter yielded an oxide which, although it did not contain any iron, possessed a yellow colour, and he found that this was due to the presence of the oxide of a new metal, which he soon afterwards detected in other samples of the oxide of zinc, as well as in metallic zinc itself. Whilst Stromeyer was engaged on these experiments, Hermann, in Schönebeck, also discovered the new metal in a sample of zinc oxide which was employed for pharmaceutical purposes, and which had been confiscated in Magdeburg, inasmuch as the acid solution yielded a yellow precipitate with sulphuretted hydrogen; this was supposed to be caused by the presence of arsenic. Hermann showed that this supposition was not correct, and ascertained that a new metal was present. Soon afterwards Meissner and Karsten also observed the existence of the same substance. In 1818 Stromeyer published a complete investigation of the metal, giving to it the name which it now bears, from *cadmia fornacum*, because the metal was chiefly found in the zinc flowers of the zinc furnaces.

Cadmium not only occurs as a constituent of zinc ores, but likewise as sulphide in the mineral greenockite, a somewhat rare substance found at Greenock, Bishopstown, and Kilpatrick in Scotland, as well as in Bohemia and Pennsylvania. The quantity of cadmium contained in the various samples of calamine and blende varies considerably. The fibrous blende found at Przibram in Bohemia contains 2 to 3 per cent., whilst the calamine of Wiesloch contains 1·6 per cent., and that of Eaton in North America 3 per cent. of cadmium.

In the process of zinc smelting the more volatile vapour of cadmium comes off with the first portions of the zinc, and these vapours burn in the air with formation of the oxides of cadmium and zinc. The cadmium is extracted from the first portion of dust which is condensed in the iron cones or other dust chambers used in connection with the adapters of the zinc furnaces, when sufficiently rich. This dust may contain from 1 to 6 per cent. of cadmium, and is mixed with a suitable proportion of coal and again distilled at a low red heat from retorts having long sheet-iron cones as adapters; the enriched distillate

thus obtained may contain over 20 per cent. of cadmium. This product is now mixed with charcoal and distilled in small cast-iron or clay retorts, and the resulting metallic cadmium is cast into rods or ingots.

Various wet methods have been suggested, and trials have been made, for the extraction of cadmium, but these methods have not come into general use.

An electrolytic method is sometimes used in the refining of the metal, the cadmium being deposited on platinum electrodes and then distilled in vacuo.

Cadmium possesses a tin-white colour and a fibrous fracture, and takes a high polish. It can be easily obtained crystallised in regular octahedra by sublimation in a current of hydrogen (Kämmerer). The pure metal obtained by electrolysing the sulphate and subliming the product in a vacuum forms flat needles or silvery six-sided plates.[1] It is somewhat harder than tin, but may be cut with a knife. It can be easily rolled out to foil and drawn into wire, but when heated to 80° it becomes brittle. When bent it emits a crackling sound, as does tin when similarly treated. The specific gravity of the cast metal is 8·546, but after hammering it attains a specific gravity of 8·667 (Schröder).[2] It melts at 321·7°[3] and boils at 778°.[4] Its vapour has a dark yellow colour and a disagreeable smell, producing headache when inhaled. The density of cadmium vapour is 3·94, and the molecule of cadmium in the gaseous state is therefore monatomic.[5]

Cadmium has been obtained in the form of a deep brown-coloured colloidal solution in water by the electrical method [6] (p. 73). In its behaviour towards acids cadmium resembles zinc.

Cadmium is employed in the preparation of certain alloys of low melting point, such as Wood's metal, which consists of eight parts of lead, fifteen of bismuth, four of tin, and three of cadmium, and melts at 60.° An amalgam of cadmium was formerly used as a stopping for teeth, but is no longer employed, as it turns the dentine yellow. Cadmium is also employed in the construction of cells of standard electromotive force.

[1] Mylius and Funk, *Zeit. anorg. Chem.*, 1896, **13**, 157.

[2] See also Kahlbaum and Sturm, *Zeit. anorg. Chem.*, 1905, **46**, 217.

[3] Holborn and Day, *Ann. Physik*, 1900, [4], **2**, 505.

[4] D. Berthelot, *Compt. rend.*, 1902, **134**, 705.

[5] Deville and Troost, *Compt. rend.*, 1859, **49**, 239. Compare Biltz, *Chem. Centr.*, 1895, i., 770.

[6] Bredig, *Zeit. physikal. Chem.*, 1900, **32**, 127.

CADMIUM COMPOUNDS.

Cadmium and Oxygen.

306 *Cadmic Oxide,* CdO.—This substance forms the brown blaze of the zinc smelters. The metal cadmium burns with a bright flame when heated in the air, forming a brown oxide, which may also be obtained by passing a mixture of steam and cadmium vapour through a red-hot tube. When the metal is heated to whiteness in a current of oxygen, the oxide sublimes in dark red, probably cubic, crystals, and may be obtained in the form of a dark blue-black powder, consisting of microscopic octahedra, by igniting the nitrate. It also occurs as a mineral [1] in octahedra possessing a specific gravity of 6·15; it does not melt at a white-heat, but is easily reduced at a moderate red-heat on charcoal before the blowpipe; the metal, however, volatilises and burns, and the oxide is deposited as a brown incrustation on the charcoal. The oxide formed by the combustion of the metal contains a trace of peroxide.[2] The reduction of cadmium oxide by carbon in an atmosphere of nitrogen commences at 580°.[3]

Cadmic Hydroxide, $Cd(OH)_2$, is obtained as a white precipitate by the addition of a soluble salt of cadmium to caustic potash. The hydroxide absorbs carbon dioxide from the air, and at 300° it is resolved into the oxide and water. It is soluble in a solution of ammonia, a complex hydroxide being probably formed,[4] as in the case of zinc hydroxide.

This oxide and hydroxide correspond to the only series of cadmium salts definitely known, which are for the most part colourless salts closely resembling those of zinc. The soluble ones have a disagreeable metallic taste, and act as emetics. A series of cadmous salts appears, however, to exist, as the cadmic halogen compounds when heated with cadmium yield salts having strongly reducing properties. These have not been obtained pure, the products appearing to consist of mixtures of cadmous and cadmic salts. If the product of the reaction of cadmium on cadmic chloride is treated with

[1] Neumann and Wittich, *Chem. Zeit.*, 1901, **25**, 561.
[2] Manchot, *Ber.*, 1906, **39**, 1170.
[3] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 419.
[4] Euler, *Ber.*, 1903, **36**, 3400; Dawson and McCrae, *Journ. Chem. Soc.*, 1900, **77**, 1239; Bonsdorff, *Zeit. anorg. Chem.*, 1904, **44**, 132.

water, lustrous transparent crystals first separate out, which soon fall to a white amorphous powder of *cadmous hydroxide*, CdOH. The latter on gently heating yields *cadmous oxide*, Cd_2O, as a yellow microcrystalline powder, which on further heating decomposes into a mixture of cadmium and cadmic oxide, the colour changing to green.[1] Suboxides are also stated to be formed when cadmium oxalate alone, or mixed with one or two molecular proportions of oxide, is heated gently, the formulæ of the oxides obtained being Cd_4O, Cd_3O_2, and Cd_2O respectively. These substances are green powders which are decomposed by dilute acids with formation of a cadmium salt and metallic cadmium, and the chief evidence of their chemical individuality is the constancy of composition of the products obtained, and the fact that in their reaction with dilute acids less heat is evolved than by the solution of a corresponding amount of cadmic oxide. When heated they change colour and a mixture of cadmium and cadmic oxide is obtained.[2]

Cadmic Salts.

307 *Cadmium Chloride*, $CdCl_2$.—This salt is obtained by evaporating a solution of the metal or oxide in hydrochloric acid. The hydrated chloride, $CdCl_2$, $2\frac{1}{2}H_2O$, is deposited in the form of rectangular prisms which readily effloresce on exposure to the air, and on heating lose water and melt at 590° (Ruff and Plato). The transparent pearly mass of the anhydrous chloride sublimes at a higher temperature in transparent micaceous laminæ. Its specific gravity at 25°/4° is 4·047.[3]

Hydrates with 5, 4, $2\frac{1}{2}$, 2 and 1 mol. H_2O have been described, but the existence of those with 5 and $2H_2O$ is doubtful (Dietz). The hydrate with $4H_2O$ passes into that with $2\frac{1}{2}H_2O$ at –5°, and the latter is converted into the monohydrate at 34°. The saturated solution contains in 100 parts of water[4]:—

At	0°	30°	60°	80°	100°
$CdCl_2$	90	128·6	136·8	140·4	147.

[1] Morse and Jones, *Amer. Chem. J.*, 1890, **12**, 488. Compare Canzoneri, *Gazz.*, 1897, **27**, ii., 486.

[2] Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 432; Tanatar and Levin, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495.

[3] Baxter and Hines, *Amer. Chem. J.*, 1904, **31**, 220.

[4] Dietz, *Zeit. anorg. Chem.*, 1899, **20**, 257.

Cadmium chloride combines with ammonia to form the unstable compound $CdCl_2,6NH_3$, a bulky powder, which passes at about 62° into $CdCl_2,2NH_3$; this may also be obtained by evaporating a solution of the chloride in aqueous ammonia[1] or of the hydroxide in ammonium chloride.[2] It is inodorous, and is stable up to 210°.

Cadmium Iodide, CdI_2, is obtained by dissolving the metal in hydriodic acid, or by digesting it with iodine and water. It crystallises in large transparent six-sided anhydrous tablets, which do not undergo alteration on exposure to the air. It melts at 350° (Ruff and Plato), and gives off iodine when heated to a higher temperature. It dissolves readily in water and alcohol. Its specific gravity is 5·61–5·73.[3] One hundred parts of water dissolve (Dietz):—

At	18°	50°	100°
CdI_2	85·3	97·4	127·6.

Iodide of cadmium is used in photography, it being one of the few iodides soluble in alcohol.

Cadmium Sulphide, CdS.—Cadmium sulphide occurs in yellow hexagonal glittering crystals as greenockite. It is obtained as a fine yellow precipitate when a cadmium salt is precipitated with sulphuretted hydrogen, this precipitate being employed as a pigment. It melts at a white heat, and forms on cooling a lemon-yellow micaceous mass, having a specific gravity of 4·86. Heated in the electric furnace, it yields crystals of greenockite.[4] It is soluble in strong hydrochloric and nitric acids, and in boiling dilute sulphuric acid.

According to Buchner,[5] two modifications of cadmium sulphide exist, the α variety is precipitated in a fairly acid solution by means of sulphuretted hydrogen, and the β variety, which resembles red lead, is precipitated in very acid solutions. This modification changes to the α form when heated.

Cadmium Sulphate, $CdSO_4$.—A concentrated solution of cadmium sulphate, when allowed to evaporate spontaneously, deposits large monoclinic crystals, having the composition $3CdSO_4,8H_2O$. This hydrate is stable in contact with its

[1] Lang and Rigaut, *Journ. Chem. Soc.*, 1899, **75**, 883.
[2] Grossmann, *Zeit. anorg. Chem.*, 1902, **33**, 149.
[3] Compare Snell, *J. Amer. Chem. Soc.*, 1907, **29**, 1288.
[4] Mourlot, *Compt. rend.*, 1896, **123**, 54.
[5] *Chem. Zeit.*, 1891, **15**, 329.

saturated solution up to 74°, at which temperature it passes into the monohydrate, a microcrystalline powder, the solubility of which diminishes with rise of temperature. A metastable hydrate with $7H_2O$ is also known.[1] The normal salt when heated yields a basic compound, $SO_2[OCd(OH)]_2$, sparingly soluble in water, and crystallising in pearly scales. One hundred parts of water at 23° dissolve 59 parts of the anhydrous normal salt, and at the boiling point a somewhat larger quantity. Crystallised cadmium sulphate is used in diseases of the eye. Stable crystalline compounds of the composition $3CdSO_4,4H_2O,4HCl$ and $3CdSO_4,8HCl$ have been described.[2]

Cadmium Nitrate, $Cd(NO_3)_2,4H_2O$, crystallises in fibrous needles, which melt at 59·5°, deliquesce in the air, and are soluble in alcohol.[3]

Cadmium Carbonates.—Minute rhombohedral crystals of the *normal carbonate*, having the sp. gr. 4·96, can be obtained by adding excess of ammonium carbonate to a solution of cadmium chloride, and then just enough ammonia to dissolve the precipitate, and heating on the water-bath.[4] The white precipitate obtained by addition of an alkali carbonate to a soluble cadmium salt possesses a varying composition, according to the temperature at which the precipitation takes place and the amount of precipitant employed. With an excess of potassium carbonate in the cold the precipitate possesses nearly the composition of the normal salt.

Detection and Estimation of Cadmium.

308 Cadmium salts do not impart any tint to the non-luminous gas-flame. The cadmium spectrum is well seen when the metal is volatilised in the electric arc; the most prominent lines being 6438 in the red, 5378 and 5338 in the green, and 5085, 4800, and 4677 in the blue.

The yellow sulphide of cadmium is the most characteristic compound of the metal. This is insoluble in dilute acids in

[1] Mylius and Funk, *Ber.*, 1897, **30**, 824.

[2] Baskerville and Harris, *J. Amer. Chem. Soc.*, 1901, **23**, 894.

[3] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 414. See also Puschin, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 382.

[4] de Schulten, *Bull. Soc. fran. Min.*, 1897, **20**, 195.

the cold, and hence may be easily distinguished from zinc as well as from the other metals already described. Cadmium sulphide can easily be distinguished from other yellow sulphides, such as those of tin, antimony, and arsenic, by its insolubility in ammonium sulphide and in the caustic alkalis. The method of separating cadmium from the other metals precipitated by sulphuretted hydrogen will be discussed under these several metals. It may suffice here to remark that cadmium hydroxide, like the corresponding copper compound, is soluble in ammonia, and that these two metals are frequently obtained together in the process of analysis. In order to separate these, two methods may be employed. In the first place potassium cyanide may be added to the blue ammoniacal solution until this becomes colourless; sulphuretted hydrogen is then passed through, when the cadmium sulphide is completely precipitated. Or, in the second place, the metals may be both precipitated as sulphides, and the washed precipitate boiled with a mixture of five parts of water and one part of concentrated sulphuric acid, which dissolves the cadmium sulphide.

The quantitative estimation of cadmium is usually made by precipitating the carbonate from the boiling solution with sodium carbonate; this is then dried and converted by ignition into the oxide, preferably on an asbestos filter in a Gooch crucible which is afterwards weighed. Cadmium may also be estimated as the sulphide, which is dried at 100° and then weighed.

Atomic Weight of Cadmium.—The atomic weight of cadmium was found by Huntingdon [1] from the analysis of the bromide to be 112·18. Morse and Jones obtained the number 112·07, but a repetition of the experiments,[2] in which allowance was made for the oxygen and nitrogen occluded by the oxide (compare Zinc, p. 663), led to the higher value 112·37. Baxter, Hines, and Freuert, by the analysis of the chloride [3] and bromide,[4] obtained the number 112·42. The determination of the atomic weight from the weight of metal electrolytically deposited from a solution of the oxide, chloride, or bromide [5] has led to the lower number 112·04, which is probably inaccurate, for Perdue and

[1] *Ber.*, 1882, **15**, 80.

[2] Morse and Arbuckle, *Amer. Chem. J.*, 1898, **20**, 536.

[3] *Zeit. anorg. Chem.*, 1905, **44**, 158.

[4] *J. Amer. Chem. Soc.*, 1906, **28**, 770.

[5] Lorimer and Smith, *Zeit. anorg. Chem.*, 1891, **1**, 364; Hardin, *J. Amer. Chem. Soc.*, 1896, **18**, 990.

Hulett,[1] from electrolytic analyses of cadmium sulphate, conclude that the atomic weight is 112·3.

The number at present (1913) accepted is 112·4.

MERCURY (HYDRARGYRUM). Hg = 200·6.

309 We do not find this metal mentioned either in the books of Moses or in the writings of the older Greek authors. Theophrastus (B.C. 300) speaks of liquid silver or *quicksilver* (χυτὸς ἄργυρος), and says that it is obtained by rubbing cinnabar with vinegar in a copper vessel. Dioscorides, in the first century, mentions this body as ὑδράργυρος (from ὕδωρ, water, and ἄργυρος, silver), and states that it is obtained by subliming cinnabar and charcoal in an iron pot, upon which a cover is luted. Pliny, who named the material thus obtained *hydrargyrum*, in contradistinction to the native mercury, to which he gave the name of *argentum vivum*, was acquainted with the fact that all solid bodies, with the exception of gold, swam on the surface of the liquid metal. Isidorus, in the beginning of the seventh century, was also acquainted with the properties of mercury, as is seen from the following extract: "Argentum vivum servatur melius in vitreis vasis, nam caeteras materias perforat."

Mercury was known to the older alchemists, who were much interested in the examination of its properties, inasmuch as they believed this body, or some substance closely resembling it, to be one of the component parts of all metals. They were acquainted with the method of purifying it by distillation, and they knew how to prepare many of its compounds. During the epoch of iatro-chemistry, the properties of the mercury compounds were more minutely examined, especially with regard to their medicinal effects. Agricola regarded mercury as a metal, but Libavius placed it amongst those "quæ metallis sunt affinia," thus connecting it with bismuth, arsenic, galena, cinnabar, and other bodies. Even at a later date many chemists held similar views; thus Brandt in 1735 spoke of it as a semi-metal, and indeed it was not reckoned as a true metal until Braune, of St. Petersburg, in the winter of the year 1759, found that it solidified when exposed to a freezing mixture made of snow and nitric acid.

[1] *J. Physical Chem.*, 1911, **15**, 155; see also Richards, *J. Amer. Chem. Soc.*, 1911, **33**, 888.

Mercury occurs in the native state, though in small quantity as compared with its other ores. It is found in globules disseminated through the native sulphide in the Palatinate, in Carniola, Hungary, Peru, California, Mexico, and other countries. It also occurs as silver- and gold-amalgam, as the iodide and chloride, and it is found occasionally in certain fahl-ores. The most important ore of mercury is the sulphide, or cinnabar. The most celebrated mercury mines are found at Idria, in

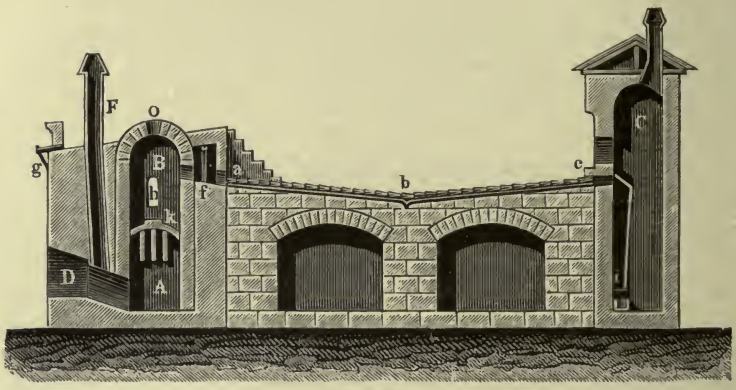


Fig. 169.

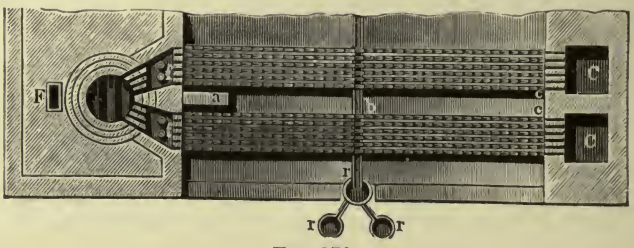


Fig. 170.

Carniola; Almaden, in Spain; in California, especially the Pioneer Mine in Napa Valley; and at Wolfsstein and Landsberg, in the Bavarian Palatinate. Cinnabar is likewise imported into this country from China and Japan.

310 Most of the mercury of commerce is obtained by the treatment of cinnabar; and the chief method of extraction is roasting with an excess of air, by which means the sulphur is oxidised to sulphur dioxide, and the metallic mercury is driven off as vapour. This roasting process is carried out in shaft furnaces, reverberatory furnaces, or muffles, and the mercury vapour is condensed in earthenware pipes, water-cooled chambers of iron, or air-cooled

chambers made of brick or wood and glass. A certain quantity of the mercury always condenses as a mercurial soot, which has to be re-treated for the extraction of the metal.

Of the older processes, in which the loss of mercury was excessive, sometimes amounting to 50 per cent., only the aludel furnace, used at Almaden, has survived. This furnace is shown in Fig. 169, and consists of a shaft B, containing a perforated arch *k*, beneath which is the fireplace A. The air necessary for oxidation enters at the fire-door D. The mercurial vapours pass through a series of six openings *f*, into tubes made of earthenware, called aludels. These are open at both ends, and fit into one another in a similar way to the condensers employed

Fig. 171.

in the manufacture of iodine. The aludels are arranged one behind the other, first in a descending, and then in an ascending position on arches of masonry (Figs. 169 and 170); the greater part of the mercury condenses in and runs from the aludels *a* (Fig. 170) into the channel *b*, and then into the cisterns *r r*. The shape and arrangement of the aludels is shown in Fig. 171. A small quantity of mercury vapour passes on into the chamber C, where it condenses, coming in contact with water contained in the vessel *i*.

The mercury thus obtained is filtered through linen, and exported, generally in iron bottles, but sometimes in leather bags.

For the treatment of finely divided ores the Granzita furnace,[1] Fig. 172, consisting of four shafts, with one fireplace (J) common to all, is used.

The shafts contain a number of inclined shelves, sloping at an angle of 45° in alternately opposite directions, to prevent the free fall of the ore. The flames from the fire together with air, pass in the opposite direction to the ore and heat the shelves. The distillation residues are removed from the furnace by means of eight openings (*u*) near the bottom, one ton being removed every 40 minutes, and a corresponding amount of fresh ore charged at the same time, by means of the hoppers (*t t*).

[1] *Eng. Min. Journ.*, 1885, 174.

The mercurial vapours are condensed by passing through brick chambers, cooled by means of cast-iron water-backs let into the sides; these are followed by towers built of glass and

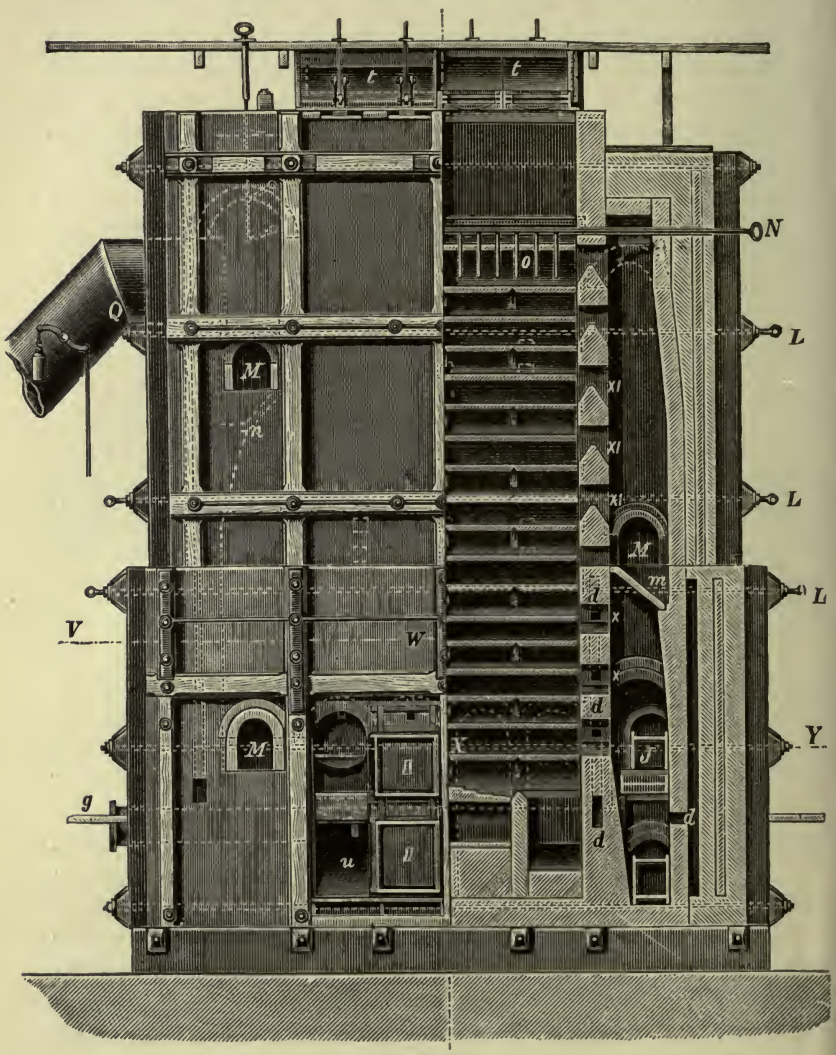
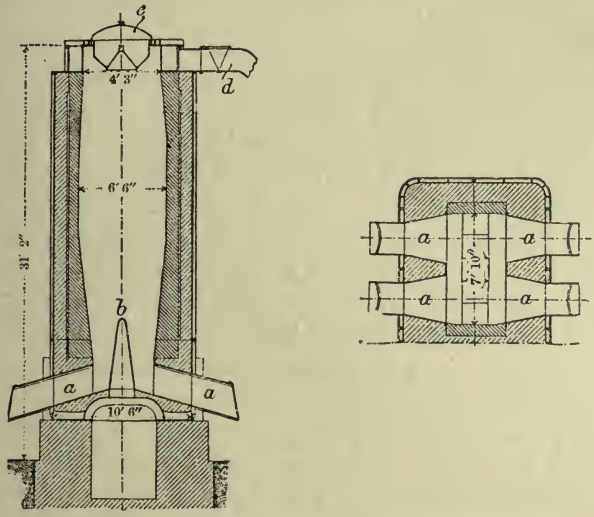


Fig. 172.

wood, and from these the gases escape into a brick tower and are finally forced into a stack by means of a fan.

For the treatment of lump ore, true shaft furnaces are now largely used, in which the ore and fuel come into direct

contact, and which are worked continuously. One of the best examples of these modern furnaces is the Novak, shown in Figs. 173, 174, in which *a* are the openings for drawing out the residues, *b* is a ridge on the bottom, containing numerous holes, through which air passes into the furnace, *c* is the charging hopper, and *d* the pipe through which the gases and vapours escape. Charcoal is the fuel generally used, and is mixed with



FIGS. 173 AND 174.

the ore before charging. The condensers usually employed consist of Y-shaped tubes of earthenware, cooled with water.

The following table shows the world's production of mercury in metric tons during the year 1910.[1]

Austria	603
Hungary	90
Italy	894
Spain	1114
Mexico	250
Russia	20
United States	763
Total	3,734

311 The mercury of commerce usually contains a certain proportion of dissolved foreign metals, and these impurities give

[1] *Mineral Industry*, 1911, **20**, 654.

rise to the "tail" seen when the metal is allowed to run over a slightly inclined surface. Impure mercury, when shaken with air, yields a black powder, caused by the oxidation of the metallic impurities, and this film of oxide incloses a small globule of the liquid metal. The surest mode of freeing mercury from these foreign metals is to distil it, the surface being covered with iron filings to prevent the spitting of the metal, which, however, cannot be completely avoided. It is a curious fact that when small quantities of lead or zinc are present in the mercury the rate of distillation is much diminished. The distillation is frequently carried out in vacuo, numerous forms of apparatus for this purpose having been proposed.[1] Mercury may be more easily purified by treating it with dilute nitric acid, the impurities being thus dissolved. For this purpose[2] the metal is allowed to flow in a very thin stream from a capillary opening in a drawn-out glass funnel into a wide glass tube 1·25 m. high and 5 cm. in diameter, which contains 5 per cent. nitric acid. A narrow tube is fastened to the bottom of this and bent upwards and then at right angles, from which the pure metal flows. The above operations may have to be repeated several times, and the metal, if pure, must leave no residue when dissolved in pure nitric acid, evaporated to dryness and ignited. It may also be purified by being placed in a long, slightly inclined tube, through which air is drawn for several days; the impurities are thereby oxidised, and separate as a scum on the surface. Purification may likewise be effected by drawing a rapid stream of air through mercury placed in a filter-flask and covered by a layer of 5 per cent. nitric acid.

Pure mercury possesses a silver-white colour. It is liquid at ordinary temperatures, and the globules retain a perfectly spherical shape. The freezing point of mercury was first determined by Hutchins in 1783, at Fort Albany, in Hudson's Bay Territory, according to instructions received from Cavendish;[3] its melting point is $-38°{\cdot}85$. In the act of freezing, mercury contracts considerably, giving rise to a solid tin-white ductile malleable mass, crystallising in octahedra, capable of being cut with a knife, and having a specific gravity of 14·1932 at its freezing point,[4] and of 14·383 at $-188°$ (Dewar).

[1] See Hulett, *Zeit. physikal. Chem.*, 1900, **33**, 611.

[2] L. Meyer, *Zeit. anal. Chem.*, 1863, **2**, 241.

[3] *Phil. Trans.*, 1783, **73**, 303. Consult Blagden, "History of the Congelation of Quicksilver," *ibid.*, 329.

[4] Mallet, *Proc. Roy. Soc.*, 1877, **26**, 77.

The liquid metal is transparent when in very thin films, and transmits violet-blue light (Melsens). When a powerful stream of water is poured from a height of a decimetre on a mass of from 15 to 20 kilos. of mercury, bubbles of the metal, of about 1 cm. in diameter, are seen swimming on the surface of the water. These consist of very thin films of mercury through which blue light is transmitted: they soon burst, and leave behind a very small solid globule of the metal.

The specific gravity of mercury at 0°/4° is 13·59545,[1] at 100° 13·3522, and at 360° 12·7405.[2] The boiling point of mercury, according to Regnault's observations, is 357°·25, the metal giving rise to a colourless vapour, which has a specific gravity, according to the experiments of Dumas, of 6·976, or according to those of Bineau, of 6·7; the molecule of mercury in the gaseous condition is, therefore, like those of zinc and cadmium—monatomic. In spite of its high boiling point, mercury volatilises perceptibly at the ordinary temperature, both in a vacuum and in air, as proved by the "silvering" of gold-leaf kept for two months in a vessel over mercury (Faraday); and Merget has shown that even at −44°, when mercury is solid, it still possesses a distinct vapour pressure. The vapour pressure of mercury, as determined by Ramsay and Young,[3] is given in the following table, the numbers below 220° being calculated by extrapolation:

Temperature. C.	Pressure in mm.	Temperature. C.	Pressure in mm.
40°	0·008	240°	56·92
80	0·092	260	96·66
100	0·270	280	157·35
120	0·719	300	246·81
140	1·763	320	373·67
160	4·013	340	548·64
180	8·535	360	784·31
200	17·015	400	1495·60
220	31·957	450	2996·06.

The vapour pressure at 0° C. probably does not exceed 0·0002 mm.

[1] Thiesen and Scheel, *Zeit. Instrumentenkunde*, 1898, **18**, 138.

[2] Landolt-Börnstein-Roth, *Physikalisch-Chemische Tabellen*, 1912, 46.

[3] *Journ. Chem. Soc.*, 1886, **49**, 37. See also Herz, *Ann. Phys. Chem.*, 1882, **17**, 193; Morley, *Zeit. physikal. Chem.*, 1904, **49**, 95.

When mercury is contaminated with oxide or its halogen derivatives it adheres to glass, forming a bright mirror (Shenstone). When shaken with different liquids, or when it is triturated with sugar, sulphur, and other bodies, the liquid metal is obtained in a very finely divided state, being converted into a grey powder. This was formerly termed *Aethiops per se.* This act of fine division is termed the "extinction" or "deadening" of mercury. Grey mercurial ointment is formed by rubbing up mercury and fat together, and in this preparation the mercury is in the form of globules having a diameter of 0·002 to 0·004 mm. Mercury is not attacked by dilute hydrochloric or sulphuric acid, but is readily dissolved by nitric acid and by hot concentrated sulphuric acid. It is readily attacked by dry chlorine, bromine, or iodine.[1]

Mercury has been obtained in the colloidal form by the reduction of mercurous nitrate by stannous nitrate in the presence of ammonium citrate, as a black precipitate which forms a deep brown solution in water.[2]

Mercury is largely used in connection with the manufacture of physical and chemical apparatus, for collecting gases which are soluble in water, for the preparation of mirror plates, for the amalgamation and extraction of silver and gold, for the preparation of the mercurial compounds, and in the electrolytic production of caustic soda.

Alloys of Mercury or Amalgams.

312 The general properties of these alloys have already been given on p. 88 of this volume.

Sodium Amalgam.—Sodium combines violently with mercury, evolving light and emitting a hissing noise. One part of sodium to 100 of mercury forms an amalgam having an oily consistency, but with 80 of mercury to 1 of sodium a pasty mass is obtained, and with smaller quantities of mercury a hard and crystalline amalgam is formed.

The existence of many compounds of sodium and mercury has been deduced from the freezing-point curve of these two elements, and some of these have been separated and analysed (p. 89). The compound of highest melting point has the formula

[1] Shenstone, *Journ. Chem. Soc.*, 1897, **71**, 483.
[2] Lottermoser, *J. pr. Chem.*, 1898, [2], **57**, 484.

$NaHg_2$, and melts at 360°, the melting point being lowered by the addition of either mercury or sodium.[1]

The amalgams of the alkali metals decompose slowly on exposure to moist air and water, and amalgamate iron and platinum. Sodium amalgam is sometimes employed in the processes of extracting silver and gold, and frequently in organic chemistry as a reducing agent.

Potassium Amalgam.—Potassium combines with mercury with evolution of heat but without incandescence, forming a silver-white compound, which is liquid when it contains one part of potassium to about seventy parts of mercury, but becomes solid when it contains more potassium. The existence of several compounds of potassium and mercury has been deduced from the thermal diagram of these elements and some of these have been separated and analysed (p. 89). The compound KHg_2, which melts at 269·8°, is the amalgam of highest melting point formed by these two elements.[2]

Ammonium Amalgam.—This compound, discovered at the same time by Berzelius and Pontin,[3] and Seebeck,[4] has already been described (p. 377).

The *Amalgams of the Alkaline Earth Metals* are easily formed by direct union of the elements, and have also been prepared by the electrolytic method (p. 89).

Magnesium Amalgam may be prepared by heating the two elements together. It decomposes water very energetically, and has been employed as a reducing agent in organic chemistry.

Copper Amalgam.—If copper foil is rubbed with a solution of nitrate of mercury it becomes covered with a bright lustrous coating of the metal, and if a line be drawn with this solution on a piece of brass foil and the foil bent at this place, it can easily be broken, as the mercury very soon penetrates the copper and renders it brittle. Copper amalgam is obtained by rubbing a copper rod with the nitrate solution, and then allowing it to remain in contact with mercury under warm water. All the copper amalgams which contain from 25 to 33 per cent. of copper, when heated to 100° become plastic when rubbed in a mortar. After from ten to twelve hours the amalgam loses its plasticity and assumes a granular crystalline structure, and is

[1] See Kurnakoff, *Zeit. anorg. Chem.*, 1900, **23**, 439; Kerp and Böttger, *ibid.*, 1900, **25**, 1; Schüller, *ibid.*, 1904, **40**, 385.

[2] Jänecke, *Zeit. physikal. Chem.*, 1907, **58**, 245.

[3] *Gilbert's Ann.*, **6**, 260.

[4] Gehlen, *Neu. Allg. Journ. Chem.*, **5**, 482.

hard enough to engrave upon tin. Its density is the same in the soft and hard states and, therefore, it does not expand or contract in hardening, and thus when hard, fills cavities into which it has been pressed in the soft state. This amalgam is used for stopping teeth, but the copper which it contains renders it objectionable on account of its tendency to blacken. It is also used for sealing bottles, glass tubes, &c., when other plastic substances, such as cork, cannot be used, as well as for taking impressions of engraved metal work.

Silver Amalgam occurs as a mineral at Moschellandsberg, in the Palatinate, and crystallises in the regular system. It is artificially prepared as the silver tree (*arbor Dianæ*) by pouring mercury into a solution of silver nitrate. The composition of the product thus deposited as well as that of the natural amalgam varies considerably (p. 89).

COMPOUNDS OF MERCURY.

313 Mercury forms two chief series of compounds, the mercuric compounds, in which the metal is divalent, and the mercurous compounds, in which each atom of the metal replaces only one of hydrogen.

The *mercuric compounds* are obtained in many cases by the action of an excess of acid on metallic mercury. They are converted by reducing agents into mercurous salts, these latter being further reduced to metallic mercury in presence of an excess of the reducing agent. The soluble salts have a metallic taste, redden blue litmus, and are extremely poisonous (see p. 690).

The molecular weights of several of these salts have been determined by the vapour density method, and by the cryoscopic and ebullioscopic methods, and have been found to be normal, corresponding with the general formula HgX^1_2.

Mercurous compounds are formed by the action of mercury or some other reducing agent on mercuric compounds, as well as in some cases by the action of acids on excess of mercury. They very readily dissociate in solution into metallic mercury and a mercuric compound,[1] this reaction being a reversible one and leading to a state of equilibrium between the mercurous

[1] Hada, *Journ. Chem. Soc.*, 1896, **69**, 1667.

and mercuric ions present. Thus, when excess of mercury is shaken with a faintly acid solution of mercuric nitrate at 25°, about 1/240 of the mercury in solution is finally present as mercuric salt and the remainder as mercurous salt, these two salts being about equally dissociated.[1]

The halogen derivatives with the exception of the fluoride are insoluble in water; the salts with oxyacids dissolve only in presence of free acid, pure water converting them into soluble acid salts and insoluble basic salts. They have a metallic taste, and are poisonous, although less so than the mercuric salts.

The true molecular formula of the mercurous compounds has been the subject of much discussion, some authorities maintaining that these compounds have the general formula HgX^{I}, and others supporting the double formula, $Hg_2X^{I}_2$. In the former case mercury in these compounds must be supposed to act as a monad, in the latter it may be present as a dyad, as shown in the constitutional formula $X^{I}{\cdot}Hg{\cdot}Hg{\cdot}X^{I}$. The vapour density of mercurous chloride corresponds with the formula HgCl, but it has been shown by Harris and V. Meyer[2] that the vapour is a mixture of mercury and mercuric chloride, formed by dissociation from the mercurous chloride. If the vapour of calomel be passed through a porous tube, the mercury diffuses through the latter and condenses in globules, whilst the portion which finally condenses inside the tube contains an excess of mercuric chloride. Further, if solid potash be placed in the vapour, it is immediately coated with yellow mercuric oxide, and does not show even a momentary formation of the dark mercurous oxide. The vapour density, therefore, cannot be taken as a proof of the molecular formula, HgCl.

Baker[3] has, however, found that very carefully dried mercurous chloride volatilises without dissociation, yielding a vapour the density of which corresponds with the formula, Hg_2Cl_2.

Beckman,[4] by cryoscopic measurements, has shown that mercurous chloride, dissolved in fused mercuric chloride, has the formula Hg_2Cl_2.

The view that the mercurous compounds contain two atoms

[1] Abel, *Zeit. anorg. Chem.*, 1891, **26**, 361.

[2] *Ber.*, 1894, **27**, 1482; 1895, **28**, 364; see also Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1541.

[3] *Journ. Chem. Soc.*, 1900, **77**, 646.

[4] *Zeit. anorg. Chem.*, 1907, **55**, 175.

of divalent mercury in the molecule is also confirmed by the work of Ogg,[1] who has shown by a study of the equilibrium between mercury, mercurous nitrate, and silver nitrate, and from various properties of solutions of mercurous nitrate, that this salt in solution yields the divalent ion Ḣg-Ḣg, and therefore probably has the formula $Hg_2(NO_3)_2$.

Mercury and Oxygen.

314 These elements form three compounds:

Mercurous oxide, Hg_2O.
Mercuric oxide, HgO.
Mercury peroxide HgO_2.

Mercurous Oxide, Hg_2O.—This compound, also called sub-oxide or grey oxide of mercury, is easily obtained by the action of caustic alkalis in excess on a mercurous salt. It is a blackish-brown powder, which by the action of light and a moderate temperature, as well as when brought in contact with different saline solutions, is decomposed into the metal and the monoxide; at 100° it unites with oxygen.[2] It corresponds to the series of *mercurous* salts.

Mercuric Oxide or *Mercury Monoxide*, HgO; commonly termed *Red Oxide of Mercury*, or *Red Precipitate*.—This compound was known to the Latin Geber, who obtained it by heating mercury in the air for a long time. It was afterwards known by the name of *mercurius præcipitatus per se*. The same compound is formed when a solution of mercury in nitric acid is evaporated, and the residue heated; the compound thus prepared was called by Raymond Lully *mercurius præcipitatus ruber*.

When mercury is exposed in a glass flask with a long neck for several weeks to a temperature somewhat below its boiling point, small red crystals of the oxide appear on the surface, and this product, which has a dark-red colour and is highly crystalline, increases gradually in quantity. Mercuric oxide is prepared on the large scale by heating an intimate mixture of mercury and mercuric nitrate until no further red fumes are given off: in this way it is obtained in the form of bright brick-red crystalline tablets, which have a specific gravity at 4° of 11·136 (Joule and Playfair).

[1] *Zeit. physikal. Chem.*, 1898, **27**, 285.
[2] Colson, *Compt. rend.*, 1899, **128**, 1104.

When a solution of a mercuric salt is precipitated by caustic potash or soda, a yellow precipitate is obtained which, when dried in the air, consists of microscopic square tablets of the anhydrous oxide. The loss of weight at 175° which led to the conclusion that this substance was a hydroxide [1] is in reality due to partial decomposition of the oxide.[2] The yellow and red oxides are regarded by many chemists as differing only in the size of their particles,[3] but according to Schoch they possess different crystalline forms, and the dissociation pressure of the yellow oxide at 300° is considerably greater than that of the red oxide. When heated at 250–600° it is converted into the red oxide with simultaneous partial decomposition into mercury and oxygen.

Mercuric oxide is a powerful poison, it possesses an unpleasant metallic taste and an alkaline reaction, and is slightly soluble in water. When heated it first changes to a dark cinnabar-red colour, and afterwards assumes a black tint, but on cooling it resumes its original appearance. At a red-heat it decomposes into its elementary constituents, and on cooling these partially recombine.

When the oxide is heated with sulphur explosions occur, and it is also decomposed when brought in contact with fused sodium, with evolution of light and heat.

Mercuric oxide is used in medicine, and is valuable for various purposes in chemical analysis.

Mercury peroxide, HgO_2, is prepared in small quantities, by the catalytic decomposition of hydrogen peroxide by means of mercury;[4] it may be prepared also by the interaction of alcoholic mercuric chloride, hydrogen peroxide, and alcoholic potash.[5] The anhydrous peroxide is an amorphous brick-red powder which is fairly stable in air. It is slowly decomposed by water.

[1] Carnelley and Walker, *Journ. Chem. Soc.*, 1888, **53**, 80.

[2] Schoch, *Amer. Chem. J.*, 1903, **29**, 319.

[3] Ostwald and Mark, *Zeit. physikal. Chem.*, 1895, **18**, 159; Ostwald, *ibid.*, 1900, **34**, 495; Koster and Stork, *Rec. trav. chim.*, 1901, ii., **20**, 394; Schick, *Zeit. physikal. Chem.*, 1902, **42**, 155. See also Cohen, *Proc. K. Akad. Wetensch., Amsterdam*, 1899, **2**, 273, 458.

[4] Antropoff, *Zeit. Elektrochem.*, 1906, **12**, 585.

[5] Pellini, *Atti R. Accad. Lincei*, 1907, [v.], **16**, ii., 408.

Mercurous Salts.

315 *Mercurous Fluoride*, Hg_2F_2, is produced by the action of HF on mercurous carbonate, or of silver fluoride on calomel.[1] It is a yellow crystalline salt, blackened by light, and soluble in water.

Mercurous Chloride, Hg_2Cl_2, is commonly known as *calomel*. Calomel occurs as a mineral termed horn-quicksilver, found at Moschellandsberg, Idria, Almaden, and other places, crystallising in rhombic prisms. The artificial substance has been known for a long time, and it appears to have been used in the sixteenth century as a medicine, known by the name of *Draco mitigatus*, *Manna metallorum*, *Aquila alba*, or *Mercurius dulcis*. It afterwards received the name calomel, which it now bears, from καλομέλας, a fine black colour, because it turns black when acted upon by an alkali.

Mercurous chloride is formed by the direct union of its elements, and also by the action of hydrochloric acid or common salt solution on a dilute solution of mercurous nitrate. In order to prevent a basic nitrate being carried down with the insoluble chloride, an excess of hydrochloric acid or salt solution must be added, and the liquid must be warmed with the precipitate for some time. In this way it is obtained in the form of a yellowish-white impalpable powder.

Calomel is commonly prepared by sublimation. For this purpose an intimate mixture of mercuric chloride (corrosive sublimate) and mercury in the right proportions is heated. Another, and now nearly obsolete process, is to rub up dry mercuric sulphate in a mortar with as much mercury as it already contains, and an equal quantity of common salt, until the globules disappear and a uniform mixture is produced. This is then sublimed, the vapour of calomel being carried into an atmosphere of steam or into a chamber containing air, where it is condensed in a finely-divided form; thus the labour of powdering it is avoided. The following decomposition occurs:

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

The sublimed powder thus obtained is well washed to free it from any traces of corrosive sublimate which it may contain, and dried ready for use. When dissolved in hot mercurous

[1] Finkener, *Pogg. Ann.*, 1860, **110**, 142.

nitrate solution, and allowed to cool, it separates out in yellowish-white tetragonal plates.

Calomel has long been known and manufactured in China and Japan under the name of *keifun* (light powder). This product occurs as a light bulky powder, consisting of very thin minute scales, lustrous, transparent, and white or faintly cream coloured. It is quite free from corrosive sublimate and is manufactured by heating balls of porous earth and salt, soaked in bittern (the mother-liquor of partially evaporated sea-water), along with mercury in iron pots lined with earth. The heat forms hydrochloric acid from the magnesium chloride in the bittern, the mercury sublimes into the clay covers of the pots, air enters by diffusion and the following reaction occurs:

$$4Hg + 4HCl + O_2 = 2Hg_2Cl_2 + 2H_2O.$$

The cover thus becomes filled with a network of micaceous particles of calomel.[1]

Calomel is tasteless, and has a specific gravity of 6·56. It evaporates at a red heat without fusion, yielding a colourless vapour, whose specific gravity is 8·21 (Deville and Troost). As already explained (p. 681), this vapour is a mixture of the vapours of mercury and mercuric chloride.

Calomel is also formed by the action of many reducing agents on solutions of mercuric chloride. It is partially decomposed by the action of concentrated solutions of chlorides, mercuric chloride passing into solution and mercury remaining undissolved.[2] The solubility of calomel [3] in water, as determined by the conductivity method, is about 0·4 mgrm. per litre at 20°.

Calomel is largely employed in medicine, the precipitated compound being more active in its medicinal properties than that prepared by sublimation, owing to its finer state of division. In certain cases abnormal poisonous effects have been produced by calomel, which have probably been caused by the presence of basic mercurous nitrate.

Mercurous Bromide, Hg_2Br_2, is obtained as a heavy white precipitate by adding hydrobromic acid or potassium bromide to mercurous nitrate solution. It is obtained in white nacreous tetragonal plates of sp. gr. 7·037 by shaking a solution of mercurous nitrate with bromine water or an alcoholic solution

[1] Divers, *J. Soc. Chem. Ind.*, 1894, **13**, 108.
[2] Richards and Archibald, *Zeit. physikal. Chem.*, 1902, **40**, 385.
[3] Ley and Heimbucher, *Zeit. Elektrochem.*, 1904, **10**, 301.

of bromine. It sublimes at 340—350° without decomposition,[1] and slowly decomposes in the light. It is only sparingly soluble in water.

Mercurous Iodide, Hg_2I_2, is prepared by rubbing mercury with mercuric iodide or iodine in the requisite proportions, and then forms a greenish-coloured powder, which is, however, not pure. If an excess of iodine is boiled with a solution of mercurous nitrate containing a little nitric acid, mercurous iodide separates on cooling in transparent yellow tetragonal plates, which gradually blacken in the light. On heating, the colour changes successively to dark yellow, orange, and garnet-red, and on cooling the same colours are observed in the reverse order; it commences to sublime at 110—120°, and melts and decomposes at 290°.[2] It is partially decomposed by heat and by treatment with potassium iodide solution into mercury and mercuric iodide.[3] It dissolves slightly in oils, the best solvent being castor oil, which dissolves 2 per cent. In the form of powder it is used in medicine.

Mercurous Sulphide does not exist, a mixture of metallic mercury and mercuric sulphide being produced in cases in which its formation might be expected.

Mercurous Sulphate, Hg_2SO_4, is formed by heating concentrated or fuming sulphuric acid with an excess of mercury, or by precipitating mercurous nitrate with sulphuric acid, or by the electrolysis of sulphuric acid with a mercury anode.[4] It is a white crystalline powder which when gently heated melts, and on cooling solidifies to a crystalline mass. It is precipitated almost completely by sulphuric acid from its solution in nitric acid. It is easily soluble in hot sulphuric acid; part of it separates out on cooling, and the remainder is precipitated on the addition of water. When heated with water at 25° it first yields the basic salt, Hg_2SO_4,Hg_2O,H_2O, as a white powder, and with a larger amount of water is converted into the oxide (Cox).

Mercurous Nitrite, $Hg_2(NO_2)_2$, is the first product of the action of nitric acid on mercury (Vol. I., p. 566), and may be prepared by the action of dilute nitric acid on excess of mercury. It forms yellow needles and is partially decomposed by water, forming mercury and mercuric nitrite, whilst part dissolves. It is

[1] Stroman, *Ber.*, 1887, **20**, 2822. [2] *Ibid.*, 2818.

[3] François, *J. Pharm.*, 1899, (6), **10**, 16; *Compt. rend.*, 1895, **121**, 888; 1896, **122**, 190.

[4] Hulett, *Zeit. physikal. Chem.*, 1904, **49**, 494.

slowly converted by dilute nitric acid into mercurous nitrate, or one of the basic salts derived from it.[1] The pure salt has a sp. gr. of 5·925.[2] When heated it decomposes, yielding nitric oxide, mercurous nitrate, mercury and mercuric oxide.[3]

Mercurous Nitrate, $Hg_2(NO_3)_2$, is formed by the action of dilute nitric acid in the cold on mercury. Hot nitric acid, on the other hand, especially if an excess of acid be employed, forms mercuric nitrate. Bergman was the first to point out the difference between the two solutions thus obtained, the explanation, according to the then prevalent views, being that the solution of the metal in cold nitric acid contained less phlogiston than that in the hot acid. At a later period the same fact was explained by stating that in the former the mercury was less strongly oxidised than in the latter case.

Mercurous nitrate crystallises in monoclinic tablets or prisms of the formula $Hg_2(NO_3)_2,2H_2O$, which lose their water on exposure to dry air. The crystals melt at 70°, forming a clear liquid of sp. gr. 4·3.[4] The pure salt is at once decomposed by water (Hada), leaving a basic nitrate. It is easily soluble in dilute nitric acid, and this solution brought on to the skin colours it, first purple, and then a black tint.

A number of different basic nitrates are formed by the action of water on the nitrate under varying conditions of temperature, concentration and acidity. Among those described [5] are $3Hg_2(NO_3)_2,Hg_2O,H_2O$, crystallising in long, thin prisms; $3Hg_2(NO_3)_2,2Hg_2O,2H_2O$, forming a white powder or hard lustrous triclinic prisms; $Hg_2(NO_3)_2,Hg_2O,H_2O$, a yellowish crystalline mass; and $Hg_2(NO_3)_2,2Hg_2O,2H_2O$, a yellowish-green powder. As already mentioned (p. 681), mercurous nitrate in solution dissociates partially into mercury and mercuric nitrate. When the salt is boiled with water, mercury slowly volatilises, and may be condensed in globules.[6]

Mercurous Carbonate, Hg_2CO_3, is obtained by precipitating the nitrate with potassium hydrogen carbonate. In order to remove a quantity of basic nitrate which is thrown down at the same time, the potassium carbonate is added in excess, and the

[1] Rây, *Zeit. anorg. Chem.*, 1896, **12**, 365; *Journ. Chem. Soc.*, 1897, **71**, 337.
[2] Rây, *Journ. Chem. Soc.*, 1908, **93**, 999.
[3] Rây and Sen, *Journ. Chem. Soc.*, 1903, **83**, 491.
[4] Retgers, *Jahrb. Min.*, 1896, ii., 183.
[5] See Cox, *Zeit. anorg. Chem.*, 1904, **40**, 174.
[6] Hada, *Journ. Chem. Soc.*, 1896, **69**, 1667.

solution is allowed to stand for some days. Mercurous carbonate is a yellow powder which decomposes at 130° into carbon dioxide, mercury, and mercuric oxide, and blackens on exposure to light (Lefort).

Mercuric Salts.

316 *Mercuric Fluoride*, $HgF_2,2H_2O$, is formed by the action of excess of hydrofluoric acid upon the oxide.[1] It is a white crystalline mass which decomposes at 50°, with formation of the yellow *oxyfluoride*, HgF(OH), which is also obtained when an excess of mercuric oxide is treated with hydrofluoric acid. On slow evaporation it separates in dark-yellow crystals. The fluoride is largely hydrolysed in aqueous solution, and is completely decomposed into oxide and hydrofluoric acid by a large amount of water at 25°, no basic salt being formed.[2]

Mercuric Chloride, $HgCl_2$.—This salt is obtained when mercury is heated in chlorine. It was first obtained by the Latin Geber according to the following receipt: "Sublime *Argentvive* thus: Rc. of it *lib.j.* of *vitriol* rubified, *lib. ij.* of *rock-allum* calcined, *lib.j* of *common salt*, *lib. semis.* and of *salt-petre* one fourth part. Incorporate all together, and sublime: and gather the *white*, *dense*, and *ponderous*, which shall be found about the *sides* of the *vessel*, and keep it, as we have appointed of other things. But if, in the first *sublimation*, you shall find it turbid, or unclean (which may happen, by reason of your own negligence), again sublime it with the same *feces*, and reserve it for use." At a later date a somewhat similar method of preparation was employed on a large scale, and the product was termed *Corrosive sublimate* or *Mercurius sublimatus corrosivus*. For this purpose an intimate mixture of 3 parts of mercury, 2 of common salt, 2 of saltpetre, and 4 of calcined ferrous sulphate was heated:

$$Hg + 2NaCl + 2KNO_3 + Fe_2S_2O_9 = HgCl_2 + Na_2SO_4 + K_2SO_4 + Fe_2O_3 + 2NO_2.$$

The nitrogen peroxide which was given off was condensed in water, and the acid obtained was employed for the preparation of mercuric oxide. At the end of the sixteenth century, corrosive

[1] Finkener, *Pogg. Ann.*, 1860, **110**, 628.

[2] Jaeger, *Zeit. anorg. Chem.*, 1901, **27**, 22; Cox, *ibid.*, 1904, **40**, 146.

sublimate was a well-known commercial article. In the works of the so-called Basil Valentine the following statement occurs. He says: "Recipe mercurii sublimati, such as can be bought at the druggists, and has been sublimed with vitriol and salt; for the ☿ takes up in the sublimation the quintam essentiam salis. Then rub down the mercurium sublimatum very finely, lay it in the cellar in a thin layer on an iron plate, let it lie for some days and nights, when a fluid will be seen to flow from it, and the ☿ is revivified."

From its strongly corrosive properties, mercuric chloride was also termed *Draco*, and as it was capable of destroying the metallic lustre of several metals, it was called *mors* or *malleus metallorum*. The process which is now employed for the manufacture of corrosive sublimate, namely, that of subliming a mixture of mercuric sulphate and common salt, was first suggested by Kunkel, who in the year 1760 described this process in his *Laboratorium Chymicum* as follows: "The best *mercurius sublimatus* for use in chemistry and such as pleases me, is when I take an oleum vitrioli, which has been highly freed from all its phlegm, with merc. viv. ana, or if it has not been rectified so well, merc. one part and oleum one and a half parts, and distil off so much oleum until all the merc. is coagulated. The white Praecipitat sublimed with Sal communis ana gives a fine corrosive sublimate."

Mercuric chloride is obtained commercially by heating a mixture of equal parts of dry common salt and mercuric sulphate. As the latter salt can only with difficulty be got free from mercurous salt, one-tenth of its weight of manganese dioxide is added to the mixture in order to prevent formation of calomel. The sublimation is carried on in large, flat, long-necked glass balloons, which are first placed in a sand-bath up to their necks, and gently heated in order to drive off all moisture. So much of the sand is then removed that only the lower half of the balloon is surrounded by sand, and then this is heated more strongly until the whole of the chloride is sublimed. On cooling, the balloon is broken and the cake of sublimate removed.

Mercuric chloride crystallises in needles belonging to the rhombic system,[1] the commercial article usually having the form of a semi-transparent crystalline crust. According to the

[1] Mitscherlich, *Pogg. Ann.*, 1833, **28**, 118; Luczizky, *Zeit. Kryst. Min.*, 1909, **46**, 297.

experiments of Poggiale, 100 parts of water dissolve the following:

At	10°	20°	50°	80°	100°
$HgCl_2$	6·57	7·39	11·34	24·3	53·96.

Mercuric chloride dissolves in about three parts of alcohol, crystallising from the solution in colourless triclinic needles, and in four parts of ether, so that when this liquid is shaken up with the aqueous solution, the greater part of the salt is removed from the water. It crystallises by sublimation in a second triclinic form.[1] Mercuric chloride undergoes electrolytic dissociation in aqueous solution only to a very slight degree,[2] but is partially hydrolysed, so that its solution has an acid reaction to litmus.[3] The aqueous solutions decompose very slowly in the dark to form mercuric oxide, chlorine, and hydrochloric acid, but in the light to form only mercurous chloride and hydrochloric acid.[4] It is precipitated from its aqueous solution by sulphuric acid,[5] but dissolves without decomposition in concentrated sulphuric and nitric acids. Its specific gravity is 5·403 (Karsten), it melts at 288° and boils at 303°, the specific gravity of its vapour being 9·8 (Mitscherlich), corresponding to the normal molecular weight. Corrosive sublimate possesses a sharp metallic taste, and is a violent poison; it is largely used, both externally and internally, in medicine, especially in cases of syphilis. It is also used as an anti-putrescent for anatomical preparations, and in dressing furs and skins, and especially as a bactericide in antiseptic surgery. The dry salt or its solution is easily reduced, first to calomel and finally to metallic mercury by arsenic, tin, zinc, &c., or by stannous chloride, oxalic acid, &c.[6]

Mercuric chloride has the power of forming crystallisable compounds with a number of other chlorides, especially with the chlorides of the alkali metals, giving rise to the following double chlorides, as well as to many others:—

$KCl,HgCl_2,H_2O$	$NaCl,HgCl_2,2H_2O$
$2KCl,HgCl_2,H_2O$	$NH_4Cl,HgCl_2$
$KCl,2HgCl_2,2H_2O$	$2NH_4Cl,HgCl_2,H_2O$
$2NaCl,HgCl_2$	$2NH_4Cl,3HgCl_2,4H_2O$.

[1] von Lang, *Wien. Akad. Ber.*, 1862, **45**, 119.

[2] Grotrian, *Ann. Phys. Chem.*, 1883, **18**, 177. See also Luther, *Zeit. physikal. Chem.*, 1904, **47**, 107.

[3] See Ley, *Ber.*, 1897, **30**, 2192.

[4] Verda, *Schweiz. Woch. Chem. Pharm.*, 1907, **45**, 179.

[5] Viard, *Compt. rend.*, 1902, **135**, 242.

[6] Oechsner de Coninck and Dautry, *Bull. Acad. roy. Bely.*, 1908, 55.

The fact that these salts dissolve in water more easily than mercuric chloride has long been known. The iatro-chemists prepared one of them by dissolving equal parts of corrosive sublimate and sal-ammoniac, and crystallising the solution. It was termed by them *Alembroth*. In many cases [1] the solutions of these double salts contain complex ions, such as $\overline{H}g\overline{Cl}_4$, &c.

Mercuric chloride also unites with hydrochloric acid [2] to form the compounds, $HgCl_2,HCl$ and $2HgCl_2,HCl$, and with phosphorus pentachloride, forming the compound $3HgCl_2,2PCl_5$, which can be sublimed in glistening needles. Compounds with hydroxylamine, acetone, and methyl alcohol have also been described.

Mercuric chloride forms also a series of basic salts or *oxychlorides*, which are obtained by the action of mercuric oxide on mercuric chloride solution, or by adding potassium hydrogen carbonate or marble [3] to the latter. The best defined of these are $2HgCl_2,HgO$, which crystallises in red monoclinic needles; $HgCl_2,2HgO$, which is a pitch-black crystalline precipitate; and $HgCl_2,3HgO$, which forms glistening golden yellow scales and occurs as the mineral kleinite in Texas.[4] In addition to these several other oxychlorides are known, containing a larger amount of oxygen.

Mercuric Bromide, $HgBr_2$.—Mercury combines with bromine with evolution of heat,[5] and the oxide dissolves in hot aqueous hydrobromic acid. The bromide dissolves to the extent of 0·4 part in 100 of cold water, and crystallises from aqueous solution in glistening scales, melting at 235°,[6] and from alcoholic solution in rhombic needles or prisms, which can easily be sublimed. It forms, with sodium bromide and chloride, the compounds $HgBr_2,2NaBr$ and $HgBr_2,2NaCl$, which are extremely soluble in water.[7]

It closely resembles the chloride and, like it, forms a number of oxysalts.[8]

[1] See Sherrill, *Zeit. physikal. Chem.*, 1903, **43**, 705.

[2] John Davy, *Phil. Trans.*, 1822, **112**, 357.

[3] Tarugi, *Gazz.*, 1901, **31**, ii., 313; Arctowski, *Zeit. anorg. Chem.*, 1896, **12**, 353.

[4] Sachs, *Sitzungsber. k. Akad. Wiss., Berlin*, 1905, 1091.

[5] Nernst, *Zeit. physikal. Chem.*, 1888, **2**, 20; Varet, *Compt. rend.*, 1895, **120**, 620.

[6] Guinchant, *Compt. rend.*, 1909, **149**, 479.

[7] Vicario, *J. Pharm. Chem.*, 1907, **26**, 145.

[8] Fischer and Wartenburg, *Chem. Zeit.*, 1902, **26**, 966.

Mercuric Iodide, HgI_2, is formed when the two elementary constituents are rubbed together in the proper proportions in a mortar with a small quantity of alcohol. It forms a scarlet crystalline powder. It is also precipitated when a solution of potassium iodide is added to one of corrosive sublimate. In this case, however, the precipitate which first forms has a pale yellow colour, but soon becomes scarlet; it is easily soluble in an excess of either liquid. Mercuric iodide crystallises in tetragonal prisms and pyramids, from solution in hot, moderately concentrated solution of potassium iodide, in boiling alcohol, or in hot nitric acid.[1] It has the sp. gr. 6·26, melts at 253—254°, and volatilises without decomposition, the vapour having the density 15·6–16·2, corresponding to the formula, HgI_2. It is very slightly soluble in water, but dissolves in many aqueous acids, ammoniacal salts, salts of mercury, and soluble iodides with which it forms soluble double compounds.

Mercuric iodide is dimorphous, for on gently heating the red modification to a temperature of 126° the mass becomes yellow with absorption of heat.[2] This change also takes place when the red crystals are melted or sublimed, yellow rhombic prisms of sp. gr. 6·06 being formed. These retain their form and colour when allowed to cool to the ordinary temperature, but readily pass into the red modification when touched or rubbed with a hard body, or even spontaneously, heat being evolved, and the red crystals retaining the form of the yellow.

Although the yellow form is stable only at and above 126°, mercuric iodide separates from nearly all organic solvents in this form at temperatures below 126°, even when crystallisation is induced by the addition of a crystal of the red form.[3] The vapour of mercuric iodide, moreover, always condenses in yellow crystals.[4]

When a cold solution of corrosive sublimate and then water are added to an alcoholic solution of potassium tri-iodide (KI_3) heated to 50°, a brown crystalline precipitate is obtained of *mercury periodide*, HgI_6. If the solutions be mixed together hot, and allowed to cool slowly, rhombic tablets of mercury periodide

[1] Luczizky, *Zeit. Kryst. Min.*, 1909, **46**, 297.

[2] Guinchant, *Compt. rend.*, 1907, **145**, 68.

[3] Kastle and Clark, *Amer. Chem. J.*, 1899, **22**, 473; Kastle and Reed, *Amer. Chem. J.*, 1902, **27**, 209; Gernez, *Compt. rend.*, 1903, **136**, 889, 1322; Mascarelli, *Atti R. Accad. Lincei*, 1906 (5), **15**, ii., 192. See also Šulc, *Zeit. anorg. Chem.*, 1900, **25**, 399.

[4] Gernez, *Compt. rend.*, 1899, **128**, 1516.

are obtained mixed with the yellow and red iodide. Mercury periodide possesses in a high degree the peculiar optical properties of tourmaline, and readily loses iodine.

Mercuric iodide forms a very large number of double salts[1] and also combines with sulphuric acid, ammonia, pyridine, and other substances. With alkali iodides and ether it forms both crystalline and liquid compounds.[2]

Mercuric Perchlorate, $Hg(ClO_4)_2$, is a deliquescent salt, crystallising with $6H_2O$. When digested with excess of mercuric oxide it yields the basic salt $2Hg(ClO_4)_2,HgO,12H_2O$, which is converted by alcohol into the compound $Hg(ClO_4)_2,2HgO$; this explodes with great violence when heated.[3] A number of other explosive substances have been obtained by the action of organic compounds on the perchlorate and chlorate.[4]

317 *Mercuric Sulphide* or *Cinnabar*, HgS, usually occurs in beds in slate rocks and shales, and more rarely in granite or porphyry. It is found in Idria, Almaden, in the Palatinate, in Carinthia, Transylvania, Tuscany, in the Urals and Altai, in China abundantly, and in Japan, Mexico, and Southern Peru. Extensive mines of cinnabar exist in California in the coast ranges at different points, from Clear Lake in the North to San Louis Obispo in the South, the principal mines in which region are at New Almaden and in the vicinity of Santa Clara Co., about sixty miles S.S.E. of San Francisco.

Cinnabar is found in rhombohedral crystals (Class 18, p. 201), which, like quartz, cause the circular polarisation of light, and also in the granular and massive states. It possesses a cochineal-red colour often inclined to brownish-red and lead-grey; its streak is scarlet, and it is sub-transparent or opaque, possesses a conchoidal fracture and adamantine lustre. Theophrastus mentions this mineral as *κιννάβαρις*; the term, however, was afterwards used to designate dragons' blood. Pliny terms this latter substance *cinnabaris*, and the mineral cinnabar, being frequently confounded with red lead, is termed by him *minium*.

The artificial preparation of this compound was first described by the Latin Geber under the name of *usifur*. At the beginning of the seventeenth century, Turquet de Mayerne found

[1] Compare Duboin, *Ann. Chim. Phys.*, 1909, [viii.], **16**, 258.
[2] Marsh, *Journ. Chem. Soc.*, 1910, **97**, 2297.
[3] Chikashigé, *Journ. Chem. Soc.*, 1895, **67**, 1013; 1905, **87**, 822.
[4] Hofmann, *Ber.*, 1905, **38**, 1999.

that by rubbing mercury and sulphur together a black powder was obtained, and in 1689 Walter Harris showed that this compound could be obtained by intimately mixing dry sulphur and mercury. Prepared in this way it was termed *Æthiops mineral*, and was employed as a medicine. In the year 1757, J. C. Jacobi proposed to employ for the same purpose the precipitate obtained by adding caustic soda to a solution of a mercury salt; this was known under the name of *pulvis hypnoticus*. The mode of preparing cinnabar by the wet way was first observed by G. Schulz, in 1687 ; he obtained it by shaking together for some time Boyle's volatile tincture of sulphur and metallic mercury. In 1773, Baumé showed that the black precipitate which this liquid produced in a solution of mercury was gradually converted into cinnabar. The difficulty of explaining the difference between the black and the red sulphides of mercury was increased by the fact that the one could be converted into the other. Stahl believed that the black compound contained more sulphur than the red one ; others assumed that in the latter compound the sulphur was more intimately combined than in the former, or that both being compounds of oxide of mercury with sulphur, the cinnabar contained mercury in a higher state of oxidation. Berthollet, on the other hand, considered cinnabar as mercury sulphide, whilst he regarded the black modification as a compound of mercury with sulphuretted hydrogen. It was not until 1833 that the identity in composition of these substances was ascertained by Fuchs,[1] and the difference between them explained by the fact that the black compound was amorphous whilst the red was crystalline.

In order to prepare cinnabar in the dry way, according to the Dutch process, mercury is added to an excess of fused sulphur and the cold broken mass brought into earthenware pots which are heated in a sand-bath until the excess of sulphur is driven off. The crucible is then covered with an iron plate, and the temperature is raised until the cinnabar sublimes and is deposited upon the plate.

In the process of manufacturing vermilion in Idria, 8 parts of sulphur and 42 parts of mercury are placed in small barrels which are caused to rotate on their axes until the contents are converted into a brown powder ; this substance is then distilled in iron retorts, furnished with a head and receiver; the purest

[1] *Schweiggers' Journ.*, 1833, 67, 1864.

cinnabar condenses in the head of the retort, whilst the portions deposited in the receiver consist of a mixture of this substance with sulphur and require redistillation. The sublimate is very finely levigated, treated with caustic soda, and then washed with water and dried.

Vermilion obtained in the wet way possesses a much finer colour than the sublimed vermilion, and it can be prepared in a variety of ways. According to Brunner's[1] process 100 parts of mercury and 38 parts of flowers of sulphur are rubbed together for some hours and then the mass is mixed with 25 parts of potash dissolved in 150 parts of water at 45°. The mixture is then heated, the quantity of water being kept constant for about eight hours. After this time it begins to exhibit a red colour, and when the right tint has been attained the mass is quickly washed with water, as by the further action of potash the vermilion becomes brown. In another process described by Firmenich,[2] 5 kilos. of mercury mixed with 2 kilos. of sulphur and 4·5 litres of a solution of potassium pentasulphide are heated in a water-bath, the potassium pentasulphide solution being obtained by reducing 20 parts of potassium sulphate with carbon and boiling the product with 3·5 parts of water and 15 parts of sulphur. The mixture is then poured into strong stoppered bottles which are well shaken whilst the liquid is being heated. After the lapse of from three to four hours a brown powder is formed. The liquid is then allowed to cool to 50°, and is digested at this temperature for some days until the colour of the product reaches the right shade: then it is mixed with caustic soda in order to withdraw the excess of sulphur, washed with water, and dried at 60°.

Sublimed cinnabar is often observed in distinct crystals having the form of the natural mineral. Generally, however, it forms a fibrous mass, having a cochineal-red colour, but when powdered it has a scarlet-red tint. Its specific gravity is 8·124 (Boullay); the specific gravity of its vapour is 5·34 (V. Meyer), from which it appears that in the gaseous condition the compound undergoes dissociation. Cinnabar is not attacked by hot nitric acid, but aqua regia dissolves it easily with liberation of sulphur. It is soluble in concentrated hydriodic acid in the cold and also in the dilute acid when warmed, sulphuretted hydrogen being evolved (Kekulé). Vermilion is used as an oil-

[1] *Pogg. Ann.*, 1828, **15**, 593.
[2] *Dingl. Polyt. Journ.*, 1864, **172**, 370.

and water-colour paint, for red lithographic and printers' ink, and for colouring sealing-wax, &c. It is sometimes adulterated with red lead or red oxide of iron. The presence of these impurities can be readily ascertained, inasmuch as pure vermilion sublimes without leaving any residue.

Black or amorphous mercuric sulphide, which occurs as a mineral in California,[1] is formed, as has already been stated, when flowers of sulphur and mercury are mixed together. The excess of sulphur can be removed by carbon disulphide, and the excess of mercury by dilute nitric acid. It is likewise formed when the component elements are gently heated together, and also by gently heating cinnabar in absence of air, although by the application of a stronger heat the latter compound again sublimes. When solutions of the polysulphides of the alkali metals act upon mercury, the black sulphide is likewise obtained, and the same compound may also be prepared by acting with an excess of sulphuretted hydrogen or sulphide of ammonium on a solution of a mercuric salt. Mercurous salts treated in this way yield a mixture of mercuric sulphide and finely divided mercury. On passing sulphuretted hydrogen into a solution of mercuric chloride, a white precipitate is first obtained, and this becomes yellow and ultimately black by the further action of the gas. This white compound has the composition $2HgS,HgCl_2$, and on sublimation decomposes into cinnabar and corrosive sublimate. Other salts of mercury form similar compounds.

Mercuric sulphide also combines with the sulphides of the alkali metals; thus, for instance, if a solution of mercuric chloride be treated with a solution of potassium sulphide containing some free alkali, a clear solution is obtained and, on evaporation, very slender silky needles of the compound HgS, $K_2S,5H_2O$ are deposited. It is a very unstable compound, and on washing is resolved into its constituents. It was first obtained by Brunner, in the preparation of vermilion according to his method. The conversion of the black amorphous sulphide into vermilion probably depends upon the formation of this body.

Mercuric Sulphate, $HgSO_4$.—This salt was known in the fourteenth century, and is obtained by heating mercury with oil of vitriol. In order to prepare a product free from mercurous salt, the mercury must be heated with 1·5 times its weight of

[1] Moore, *J. pr. Chem.*, 1870, [2], 2, 319.

sulphuric acid, and evaporated to dryness. In this way a white opaque mass is obtained, which crystallises from an excess of sulphuric acid in small stellate plates, having a silvery lustre. When gently warmed it becomes yellow and afterwards red-coloured, and decomposes, when strongly heated, into mercury, oxygen, sulphur dioxide, and mercurous sulphate. Water decomposes it even at 25° with formation of the insoluble basic salt, $3HgO,SO_3$, a heavy lemon-coloured powder which on heating becomes of a red colour, and dissolves in 2,000 parts of cold, and 600 parts of boiling, water. The basic compound was described by Basil Valentine, and was used by the iatro-chemists under the name of *turpetum minerale*. This appears to be the only definite basic mercuric sulphate which exists at 25°.[1]

Mercuric sulphate forms several compounds with hydrogen chloride.[2]

318 *Mercury Nitride* or *Trimercuric-diamine*, N_2Hg_3.—For the preparation of this compound, a solution of mercuric iodide or bromide in liquid ammonia is added to an excess of potass-amide dissolved in the same solvent:

$$3HgI_2+6KNH_2=Hg_3N_2+6KI+4NH_3.$$

It is a chocolate-brown powder, which in the dry state is very explosive. Aqueous acids and solutions of ammonium salts in liquid ammonia readily dissolve it.[3]

The statement [4] that the nitride is formed by the action of ammonia on mercuric oxide at 130° has not been confirmed.[5]

Mercuric Nitrate, $Hg(NO_3)_2$.—This salt was classed among the vitriols by the alchemists, and its preparation is thus described in the works of Basil Valentine:

"Vitriolum mercurii is easily made with an *aqua fort* distilled from saltpetre, and alum *ana*; if it is dissolved in it, crystals like a vitriol shoot out; these are then ablued and purified with *spiritus vini*, which previously has been rectified with *sal tartari*; thus it is made into a sweet oil. This is a noble medicine *ad luem gallicam*, it cures all sores, consumptions, disuries, gouts and drives out many other diseases from the human body."

[1] Cox, *Zeit. anorg. Chem.*, 1904, **40**, 165. See also Hoitsema, *Zeit. physikal. Chem.*, 1895, **17**, 651; Guinchant, *Bull. Soc. chim.*, 1896, [3], **15**, 555.

[2] Baskerville and Weil, *J. Amer. Chem. Soc.*, 1901, **23**, 894.

[3] Franklin, *Zeit. anorg. Chem.*, 1905, **46**, 1.

[4] Plantamour, *Annalen*, 1841, **40**, 115.

[5] Hofmann and Marburg, *Annalen*, 1899, **305**, 204.

In order to prepare this salt, mercury is boiled with nitric acid until a portion of the liquid no longer gives a precipitate with common salt. On evaporating the solution over sulphuric acid large crystals separate out having the formula $2Hg(NO_3)_2,H_2O$. The same salt, which is very deliquescent, is obtained as a crystalline magma, by adding strong nitric acid to the concentrated solution. The mother-liquor from the large crystals is a thick liquid which possesses the power, first noticed by Libavius, of colouring the skin a dark-red tint. On evaporating the solution, a basic salt, $2Hg(NO_3)OH,H_2O$, separates out in long transparent prisms which possess a metallic, but not an acid taste.

When mercuric nitrate is treated with water at 25° it yields the basic salt, $Hg(NO_3)_2,2HgO$, as a heavy, white powder, which is decomposed by the further action of water, leaving mercuric oxide.[1]

Mercuric Nitrite, $Hg(NO_2)_2$, is obtained by the action of mercuric chloride on silver nitrite or by the decomposition of mecurous nitrate by water.[2]

Mercuric Hyponitrite, HgN_2O_2, is prepared by the action of sodium hyponitrite on mercuric nitrite, and is a light buff-coloured powder. It decomposes spontaneously into nitric oxide and mercurous hyponitrite, and is the only mercuric salt which decomposes into a mercurous salt.[3]

Mercuric Phosphide is obtained as a black powder, together with mercuric phosphate, by heating mercuric oxide and phosphorus together in water. If a current of gaseous hydrogen phosphide is passed over gently heated mercuric chloride, an orange-yellow sublimate of mercuric phosphide is obtained which decomposes into its elements on heating (H. Rose). The phosphide, Hg_3P_4, is obtained in hexagonal prisms when mercury is heated with phosphorus di-iodide. It is readily decomposed by heat.[4]

Mercuric Arsenide, Hg_3As_2, is the final product obtained when a mixture of arsine and hydrogen is passed into an alcoholic solution of mercuric chloride. It is a black powder which oxidises in the air, forming arsenious oxide and mercury.[5]

[1] Cox, *Zeit. anorg. Chem.*, 1904, **40**, 159.

[2] Rây, *Journ. Chem. Soc.*, 1897, **71**, 341.

[3] Divers, *Journ. Chem. Soc.*, 1899, **75**, 119. See also Rây, *ibid.*, 1907, **91**, 1404; Rây and Gañguli, *ibid.*, 1399.

[4] Granger, *Journ. Chem. Soc.*, 1898, **74**, ii., 474.

[5] Partheil and Amort, *Arch. Pharm.*, 1899, **237**, 121.

319 *Mercuric Acetylide*, $3C_2Hg,H_2O$, is best prepared by passing acetylene into a solution of mercuric oxide in ammonia and ammonium carbonate. It is a heavy white powder, which explodes when rapidly heated. When heated with hydrochloric acid a mixture of acetylene and acetaldehyde is produced.[1]

When acetylene is passed into a solution of mercuric nitrate derivatives of acetaldehyde are formed, which are decomposed by acids with formation of acetaldehyde, no acetylene being liberated.[2]

Mercuric Carbonates.—Only basic mercuric carbonates are known. If a solution of mercuric nitrate is poured into an excess of potassium carbonate solution, a dark brown precipitate of $HgCO_3,2HgO$ is formed, and if a solution of potassium bicarbonate is employed, an amorphous brown precipitate of $HgCO_3,3HgO$ is formed.

Mercuric Cyanide, $Hg(CN)_2$.—This compound was discovered by Scheele, who obtained it by boiling Prussian blue with mercuric oxide and water. It is formed also by dissolving mercuric oxide in dilute hydrocyanic acid, or by boiling one part of potassium ferrocyanide with two parts of mercuric sulphate and eight parts of water:

$$2K_4Fe(CN)_6+7HgSO_4=6Hg(CN)_2+4K_2SO_4+Fe_2(SO_4)_3+Hg.$$

It may be prepared by adding a solution of sodium cyanide to mercuric sulphate.[3]

Mercuric cyanide dissolves in eight parts of cold water and crystallises from the hot aqueous solution in white needles or transparent tetragonal prisms which are insoluble in absolute alcohol. The salt is only dissociated to a very minute extent in aqueous solution, and hence its solution does not yield all the reactions characteristic of mercuric ions; thus its solution gives no precipitate with caustic soda or potassium iodide. It is however, decomposed by sulphuretted hydrogen and by boiling with hydrochloric, hydrobromic, hydriodic, and dilute sulphuric acids, hydrocyanic acid distilling over. It forms crystalline double compounds with many other salts. In aqueous solution, it yields with potassium iodide the complex salt,

$$Hg(CN)_2,HgI_2,2KCN.$$[4]

[1] See Plimpton and Travers, *Journ. Chem. Soc.*, 1894, **65**, 264, where references to the earlier literature are to be found.

[2] Hofmann, *Ber.*, 1898, **31**, 2212, 2783. See also Erdmann and Köthner, *Zeit. anorg. Chem.*, 1898, **18**, 54.

[3] Rupp and Goy, *Apoth. Zeit.*, 1908, **23**, 374.

[4] Rupp and Goy, *Arch. Pharm.*, 1909, **247**, 100.

When heated it decomposes into cyanogen and metallic mercury. Its aqueous solution readily dissolves mercuric oxide, and on evaporating the alkaline solution thus obtained, small needles of a basic cyanide, $Hg(CN)_2,HgO$, are formed. This is known as *mercuric oxycyanide*, and is used as an antiseptic.[1]

Mercuric Cyanate, $Hg(OCN)_2$, and *Mercuric Thiocyanate*, $Hg(SCN)_2$, are white crystalline precipitates. In order to prepare the latter salt a solution of ammonium thiocyanate is precipitated with excess of corrosive sublimate solution. This compound is used for the preparation of the so-called Pharaoh's serpents. The dried precipitate is rubbed up with gum-water to a thick plastic mass, and short cones are formed of this mixture, which are then dried. On igniting them at the end they burn with a blue sulphur-like flame, the ash being very bulky and extending in a serpent-like form.

Ammoniacal Compounds of Mercury.

320 Many different series of ammoniacal derivatives of mercury have been described, but very little is known as to their constitution. Most of the derivatives are insoluble in the ordinary solvents and cannot be volatilised without decomposition, so that their molecular weights cannot be determined. Rammelsberg[2] formulated all these compounds as derived from dimercurammonium salts, in which two atoms of mercury replaced the four hydrogen atoms of the ammonium radical. Many serious objections to this view have been urged by other investigators,[3] and it seems probable that substitution products both of ammonia (aminomercuric compounds) and of ammonium compounds (mercuriammonium compounds) exist, as well as compounds formed by the additive combination of ammonia with mercuric salts. No ammoniacal mercurous compounds appear to have been obtained. Thus the supposed mercurous ammonium derivatives are mixtures of mercuric derivatives and finely divided metallic mercury, which latter gives them a black colour.

[1] See Holdermann, *Arch. Pharm.*, 1905, **243**, 600; 1906, **244**, 133; Rupp, *ibid.*, 1906, **244**, 1.

[2] *J. pr. Chem.*, 1888, [2], **38**, 558. See also Barfoed, *J. pr. Chem.*, 1889, [2], **39**, 201; Pesci, *Gazz.*, 1891, **21**, 569; *Zeit. anorg. Chem.*, 1899, **21**, 301.

[3] Hofmann and Marburg, *Annalen*, 1899, **305**, 198; *Zeit. anorg. Chem.*, 1900, **23**, 126; Franklin, *J. Amer. Chem. Soc.*, 1907, **29**, 35.

Millon's Base.—When mercuric oxide is gently warmed with pure dilute ammonia, a pale yellow powder having the composition $H_5O_3NHg_2$ is obtained, which deflagrates without explosion on rubbing, or when thrown on to hot charcoal. This compound is known as Millon's base and is variously formulated as $(HOHg)_2NH_2{\cdot}OH$ (Hofmann and Marburg), or $NHg_2{\cdot}OH,2H_2O$ (Rammelsberg). When exposed over caustic potash in an atmosphere of ammonia it loses water, yielding the dark yellow compound $(OHg_2)NH_2{\cdot}OH$. This substance and Millon's base both yield salts when treated with acids. When, however, the compound $(OHg_2)NH_2{\cdot}OH$ is heated at 125° in a current of ammonia, a second molecule of water is lost, and a non-basic highly explosive dark-brown powder of the composition NHg_2OH is produced, which is also formed when ammonia is passed over dried yellow mercuric oxide at 120°, and is known as *dimercuriammonium hydroxide.* The formation of the anhydrous oxide, $(NHg_2)_2O$, described by Weyl [1] as a product of the dehydration of Millon's base, has not been confirmed (Hofmann and Marburg).

Salts of Millon's Base are formed when ammonia is added to mercuric salts of oxyacids, and when the base is digested with 6 per cent. aqueous solutions of the acids. These salts have as a rule the empirical formula $H_2ONHg_2X^I$, and, like the base, have been formulated in two different ways—as oxydimercuriammonium salts, $(OHg_2)NH_2{\cdot}X^I$, or as dimercuriammonium salts, NHg_2X^I,H_2O. Anhydrous salts of the formula NHg_2X^I have also been prepared by the action of liquid ammonia or potassamide on mercuric bromide and iodide, but it is probable that these substances are not true derivatives of Millon's base, but are amino-compounds of the constitution Hg:N·HgX (Franklin [2]). Compounds of the same composition have been described by François [3] and by Pesci [4] as formed by the action of aqueous ammonia on mercuric iodide and bromide.

The Chloride of Millon's Base, $(OHg_2)NH_2{\cdot}Cl$, or NHg_2Cl,H_2O, is formed by the action of hydrochloric acid on Millon's base, and may be prepared by digesting infusible white precipitate with a large amount of water at 60–70°. It forms a yellowish powder, which is stable in an atmosphere of ammonia at 125°, but

[1] *Pogg. Ann.*, 1864, **121**, 601. [2] *Zeit. anorg. Chem.*, 1905, **46**, 1.

[3] *Compt. rend.*, 1900, **130**, 332, 1022.

[4] Compare, however, Hofmann and Marburg, *Annalen*, 1899, **305**, 191.

decomposes at 180° with separation of mercury (Hofmann and Marburg).

The Iodide of Millon's Base, $(OHg_2)NH_2{\cdot}I$, which is frequently described as oxydimercuriammonium iodide, is formed by the action of an excess of ammonia on mercuric iodide, and also when ammonia is passed at a temperature of 180° over the basic oxy-iodide of mercury, $HgI_2,3HgO$.

The same compound is easily obtained by adding ammonia to a solution of mercuric potassium iodide, containing an excess of potash, and hence this liquid, known as Nessler's solution (Vol. I., p. 330), is employed as a very delicate reagent for the detection of ammonia. It is a brown powder which often exhibits a reddish-purple colour, and, on heating in absence of air, fuses to a brown liquid, whilst when more strongly heated, it decomposes with emission of light, into water, mercuric iodide, ammonia, and nitrogen.

Infusible White Precipitate, which appears to have been first prepared by Lemery, is formed when a solution of mercuric chloride is precipitated by ammonia, and has the empirical formula $NHgH_2Cl$. It is formed also by the action of liquid ammonia and of potassamide on mercuric chloride (Franklin). It is a bulky white powder having an earthy metallic taste, and is insoluble in water, but on long-continued washing or on treatment with caustic potash it becomes yellow, owing to partial decomposition with formation of the yellowish-coloured chloride of Millon's base. It decomposes below a red heat without fusion, forming calomel, ammonia, and nitrogen:

$$6NH_2HgCl = 3Hg_2Cl_2 + N_2 + 4NH_3,$$

and on warming with ammonium chloride yields the fusible white precipitate described below. If it is mixed with iodine and alcohol is poured on to it, mercuric iodide is first formed and then a violent explosion occurs. This mixture also deflagrates in the dry state after some time.

The constitution of this substance has given rise to much discussion. Rammelsberg and Pesci regard it as a double salt of dimercuriammonium chloride and ammonium chloride, NHg_2Cl, NH_4Cl, whereas Hofmann and Marburg, and Franklin assign to it only half this molecular weight, formulating it as $NH_2{\cdot}HgCl$, or aminomercuric chloride. The latter view is supported by the existence of an analogous compound derived from ethylamine, $NH_2C_2H_5$, which has the formula NHC_2H_5HgCl, and resembles

infusible white precipitate in properties, although ethylamine is incapable of yielding a compound corresponding with Rammelsberg's formula.

Fusible White Precipitate.—This compound was first prepared by Raymond Lully, by precipitating mercuric nitrate with sal-ammoniac and salt of tartar. He was acquainted with its property of fusing when heated. At a later time this body was confounded not only with the foregoing compound, prepared first by Lemery, but also with calomel prepared by the wet process. Kunkel, although he gave both to this last preparation and to fusible white precipitate the name of *lac mercurii*, was aware of their difference. He says, "Whether these two have the same effect in medicine, I leave to the physicians and surgeons; *in examine chymico* they are very different." Wöhler, in 1838, pointed out the difference between the fusible and infusible precipitate.

Fusible white precipitate is obtained either by adding a solution of corrosive sublimate to a boiling aqueous mixture of sal-ammoniac and ammonia as long as the precipitate which is formed dissolves, or by boiling the infusible white precipitate with a solution of sal-ammoniac. Small regular dodecahedra or crystalline crusts are deposited on cooling. The compound fuses on heating, losing nitrogen and ammonia, whilst a mixture of calomel, corrosive sublimate, and sal-ammoniac sublimes.

It has the empirical formula $N_2H_6HgCl_2$, and has been formulated as the double salt, $NHg_2Cl,3NH_4Cl$, or as the additive compound, $Hg(NH_3)_2Cl_2$. As in the case of the infusible white precipitate an analogous derivative of ethylamine is known, a fact which is in favour of the latter formula.

Mercuriphosphonium compounds analogous to the above mercuriammonium salts have also been prepared.

Therapeutic Uses of Mercury and its Compounds.

321 The poisonous effects of mercury were known to Dioscorides and Pliny, and it appears that even in those days mercurial preparations were employed as medicines. From that period up to the fifteenth century, mercury was but sparingly used in medicine, and then for external purposes only. Even in the fifteenth century, the outward use of mercurial compounds was discountenanced by the then prevailing schools of medicine, and at the beginning of the sixteenth century the few physicians

who had dared to employ mercurial ointment were vigorously assailed. The employment of mercurial preparations was, however, soon afterwards introduced by Paracelsus, and by degrees became common.

Metallic mercury rarely leads to toxic phenomena when taken internally. Large quantities (several pounds) used to be given to overcome intestinal obstruction, and when the mere weight of the liquid metal was sufficient to remove the obstruction mechanically, the mercury passed through the intestines rapidly and was excreted without any absorption. In small quantities, especially if it be in a state of fine division, mercury is rapidly absorbed, and exercises medicinal or toxic effects according to the quantity employed. Metallic mercury can be absorbed through the unbroken skin, and may lead to local disturbances (dermatitis) and to general toxic symptoms, and mercury vapour is frequently the cause of severe forms of poisoning.

The salts of mercury are poisonous. In some respects, the poisonous action of mercury compounds resembles that of salts of other heavy metals, but a special action on the animal economy lends an important therapeutic value to these salts. In general, mercury is employed therapeutically both for local and general inflammations, the disease for which it is most valuable being syphilis.

Calomel, Hg_2Cl_2, corrosive sublimate, $HgCl_2$, and mercuric iodide, HgI_2, are most commonly used. In the intestines, small quantities of calomel may be completely absorbed and give rise to poisonous symptoms while larger quantities, acting as a purgative, are less dangerous; as a rule, from 0·032 to 0·32 gram is the dose used in medicine. It is supposed that calomel is acted upon by the sodium chloride present in the body, forming mercuric chloride and metallic mercury, while some authors believe that oxychlorides are also formed.

Corrosive sublimate, when in concentrated solution, acts as a powerful caustic. In small doses, it produces severe toxic symptoms, and only in very small quantities is it tolerated therapeutically. Even 0·1 gram, when rapidly absorbed, is a fatal dose. The iodide acts similarly.

When small quantities of mercury are absorbed daily for a prolonged period, a complex of symptoms, known as mercurialism, appears. These include salivation, ulceration of the mucus membranes of the mouth, tremors, nervous symptoms, headache, anæmia and wasting.

Chronic mercurial poisoning is met with in those who habitually work with the metal, namely, miners in quicksilver mines, persons engaged in extracting gold by the amalgamation process, and those engaged in making mirrors, thermometers, barometers, &c.

Detection and Estimation of Mercury.

322 Bunsen's flame-reaction may be conveniently employed in order to detect the presence of mercury in a solid body. For this purpose the substance is mixed with a small quantity of anhydrous sodium carbonate and nitre, and the mixture is heated in a tube held in the flame by means of a platinum wire wound round it, the mouth of the tube being placed directly under a small porcelain basin filled with cold water. The mercury is then volatilised, and condenses on the cool lower surface of the porcelain basin in the form of a grey film. This is wiped off with a small piece of filter paper, when the minute globules of liquid metal are rubbed together and a larger globule is obtained. If a large quantity of mercury be present, globules are at once formed on the cold basin.

A similar film can be more simply obtained by heating the compound on a piece of asbestos in the reducing zone of the flame beneath a porcelain basin. The metal may also be detected by heating the compound in a bulb tube with sodium carbonate and potassium cyanide, the mercury being deposited on the cool part of the tube.

When a liquid has to be tested for mercury, it is in the first place acidified with hydrochloric acid. If this produces a white precipitate a mercurous salt may be present together with silver, lead, and thallium. The last two metals may be removed by boiling the precipitate with water. The residue is then treated with ammonia, in which the chloride of silver is soluble. If a black powder remains mercury is present, and its presence can be confirmed by the flame reaction just described. The filtrate from the first precipitate, or the solution in which the hydrochloric acid gives no precipitate, is saturated with a current of sulphuretted hydrogen gas. If mercury is present, a white precipitate will first be formed, but this rapidly changes colour, becoming yellow, brownish-red, and finally black. In order to separate mercury from the other sulphides which may be present, the precipitate is first washed with hot

water, then warmed with sulphide of ammonium, again washed with water, and the residue treated with hot dilute nitric acid. If a heavy black powder remains undissolved, this is treated with aqua regia, the solution concentrated, and stannous chloride added to this solution, when calomel is precipitated; if an excess of the precipitant is added, finely divided metallic mercury is deposited as a black powder, which on boiling with hydrochloric acid unites to form distinct globules. The following equations represent the decomposition:

$$(a)\ 2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4,$$
$$(b)\ Hg_2Cl_2+SnCl_2=2Hg+SnCl_4.$$

The spark spectrum of mercury contains a large number of lines, and has been carefully mapped by Huggins, and Hartley and Adeney.[1]

Mercury is best estimated quantitatively by precipitating the solution with sulphuretted hydrogen. The sulphide thus precipitated frequently contains free sulphur, and it is therefore warmed with hydrochloric acid, nitric acid being added drop by drop until the sulphur, which separates out, has become yellow. Then the solution is diluted with water, nearly neutralised with caustic soda, excess of potassium cyanide added, and the sulphide again thrown down with sulphuretted hydrogen; the precipitate thus obtained is quickly washed with cold water, dried at 100° and weighed. The sulphur may also be removed by washing the precipitate with alcohol to remove water, and then with carbon disulphide. Mercury is also sometimes estimated in the form of mercurous chloride, or as the free metal obtained by distillation with lime or iron, or by electrolysis of a solution of the cyanide in potassium cyanide, or better by the electrolysis of acid solutions with a mercury cathode.

Atomic Weight of Mercury.—The atomic weight of mercury was determined by Turner,[2] and by Erdmann and Marchand,[3] by the analysis of mercuric oxide, and also by the latter investigators by the analysis of the sulphide. Millon[4] and Svanberg[5] estimated the quantity of mercury formed by heating the chloride with lime in a current of hydrogen. Hardin[6] compared the weights of silver and mercury deposited by the same current,

[1] See Watts, *Index of Spectra*, p. 105 (Heywood, Manchester, 1889).
[2] *Annalen*, 1835, **13**, 14.
[3] *J. pr. Chem.*, 1844, **31**, 385.
[4] *Compt. rend.*, 1845, **20**, 1291.
[5] *Jahresb.*, 1847–8, 445.
[6] *J. Amer. Chem. Soc.*, 1896, **18**, 990.

and also effected the electrolytic analysis of mercuric chloride, bromide, and cyanide, arriving finally at the value 199·93.

Easley obtained a higher figure (200·48) by reducing mercuric chloride by means of hydrogen peroxide and partly by electrodeposition. At the same time from the ratio $HgCl_2$: 2AgCl, he obtained the figure 200·62.[1] Later he obtained the value 200·63 by the analysis of the chloride,[2] and by the analysis of the bromide, 200·64.[3] The value at present (1913) accepted is 200·6.

[1] *J. Amer. Chem. Soc.*, 1909, **31**, 1207. [2] *Ibid.*, 1910, **32**, 1117.
[3] Easley and Braun, *J. Amer. Chem. Soc.*, 1912, **34**, 137.

GROUP III.

Sub-Group (*a*)—Boron and the Rare Earth Metals.

Boron.
Scandium.
Yttrium.
Lanthanum.

Sub-Group (*b*)—The Aluminium Group of Metals.

Aluminium.
Gallium.
Indium.
Thallium.

323 These elements all form oxides of the formula R_2O_3, and unite with the halogens to form compounds of the type RX_3 or R_2X_6.

Boron hydroxide behaves as an acid to most bases, and acts as a base only towards the strongest acids, but the basic character of the oxides becomes more marked in this group as the atomic weight increases. The oxides of the metals of sub-group (*a*) are, as in the second group, more basic than those of sub-group (*b*). Thus the latter form salts with strong alkalis, whereas the former do not.

The element boron, being the least electropositive element of the group and usually occurring in an anion, has already been described among the non-metals (Vol. I., p. 713). Since the chemical relations of the rare earth metals are so little known at present, the metals of sub-group (*a*) are described along with the other rare earth metals.

THE ALUMINIUM GROUP.

324 These metals are permanent in the air at ordinary temperatures, but become oxidised when strongly heated in air or oxygen. The volatility of the metals increases with the atomic weight, and the same order is observed in the ease of reduction from the oxide. Thus indium and thallium both yield an incrustation of the oxide and a metallic bead, when their compounds are reduced on charcoal, whereas aluminium compounds do not give this reaction.

All these metals have small atomic volumes, and occur just after the minima on Lothar Meyer's diagram (p. 60). They are all malleable and fusible, and form typical hydroxides which act as weak bases, the corresponding salts being often readily decomposed by boiling with water. These hydroxides also act as weak acids towards strong bases. Thus the hydroxide of gallium is soluble both in potash and ammonia, and those of aluminium and of indium in potash, whilst thallic hydroxide is insoluble in alkalis.

Aluminium, gallium, and indium form characteristic double sulphates of the formula $M_2SO_4,R_2(SO_4)_3,24H_2O$, known as the alums, in which M represents a monovalent metal. Similar compounds have not yet been obtained from thallium. Both aluminium and thallium yield organo-metallic derivatives.

Special interest attaches to the position of gallium in this group, because its properties and relations to aluminium and indium show that it is identical with the "eka-aluminium" of Mendeléeff, the existence of which was predicted by that chemist four years before the actual discovery of the element by Lecoq de Boisbaudran (p. 68).

In addition to compounds of the type RX_3, lower chlorides of indium and gallium are also known, whilst thallium forms a whole series of salts in which it acts as a monovalent metal. These salts are more stable than those which correspond in type to the aluminium salts and bear a remarkable chemical resemblance to the salts of the alkali metals, with which they are in many cases isomorphous. Physically, the metal thallium closely resembles lead, which occupies the corresponding place in Group IV, and its compounds with the halogens (except fluorine) and sulphur are very similar in properties to the corresponding lead compounds. In consequence of this remark-

able behaviour, Dumas, on the occasion of the discussion of Lamy's investigation in the French Academy, termed it the ornithorhynchus amongst the metals.

ALUMINIUM. Al = 27·1.

325 The name of this metal is derived from *alumen*, alum. This, as well as the corresponding Greek word (*στυπτηρία*), was originally used to designate very different bodies, all of which possessed the common property of an astringent taste. There can, however, be little doubt that alum itself was included amongst these bodies, and this salt was well known to the Latin Geber and the later alchemists, being, however, classed amongst the vitriols, until Paracelsus showed that it differed from this last family of salts. In his second treatise, *De Generibus Salium*, he states: "Alum is in no wise connected with the metals, but is a salt, standing alone in the acid, and taking its *corpus* from the intermixture of the earths; vitriol does not do so, but solely from the intermixture of metallic *corpora*." The nature of the earth, which is combined in alum with sulphuric acid, remained long undetermined. It was usually supposed to be a calcareous earth, although it was noticed in the seventeenth century that clay, when treated with sulphuric acid, gave an alum: and hence Pott, in his *Lithognosy*, published in 1746, stated that the basis of alum was an argillaceous earth. It was not till 1754 that Marggraf showed that alumina differed totally in its properties from lime, and that clay contained this earth, combined with silica.

Davy, as well as other chemists, endeavoured to decompose alumina into its elements, as it was generally acknowledged to be an oxide. The results they obtained were, however, but unsatisfactory, and Wöhler, in 1827, was the first to prepare pure aluminium.

Of all the elements, with the exceptions of oxygen and silicon, aluminium is the most widely distributed, and contained in the largest quantity in the solid crust of the earth. It occurs as the oxide, Al_2O_3, in the mineral corundum, of which the ruby and sapphire are varieties. It is found more commonly as diaspore, $Al_2O_4H_2$, and bauxite, a hydrated aluminium oxide in which varying portions of aluminium are replaced by iron, whilst it occurs in far larger quantity in combination with silica, forming

a great variety of double silicates, amongst which potash-felspar or orthoclase, $(K,Na)AlSi_3O_8$, may be mentioned as being most important, as this forms the chief constituent of granite, gneiss, syenite, porphyry, trachyte, &c. Soda-felspar or albite, and lime-felspar or labradorite, also occur in large quantities. Amongst other important double silicates we find the garnet group. The several members of this group are named from the different isomorphous metals which they contain; thus, for instance, we have lime-alumina garnet or grossular, $Ca_3Al_2(SiO_4)_3$; iron-alumina garnet, or almandine, $(Fe,Mg)_3Al_2(SiO_4)_3$; lime-iron garnet, or andradite, $Ca_3Fe_2(SiO_4)_3$. The group of micas also contains a large number of important minerals, as common mica or biotite, $K_2HAl_3(SiO_4)_3(Mg,Fe)_6(SiO_4)_3$; and chlorite or ripidolite, $H_9(Fe,Mg)_5Al_3Si_3O_{20}$, the latter compounds forming the chief constituent of many slate rocks.

Aluminium occurs also in large quantities as cryolite, a double fluoride of aluminium and sodium, Na_3AlF_6, the name being derived from the ice-like appearance of the mineral, which is largely worked in Greenland and has served as an industrial source of the metal.

The weathering of felspar gives rise to porcelain-clay, china-clay, or kaolin, $Al_2Si_2O_7,2H_2O$, whilst the different varieties of coloured clays are obtained from a similar disintegration of felspathic rocks containing iron.

Although alumina is largely contained in all fertile soil, it is found only in small quantity in most plants.[1] Certain cryptogams, however, especially the species of lycopodium, take it up largely. Thus the ash of *L. Clavatum* contains up to 26·65, and that of *L. Chamaecyparissus* even as much as 57·26 per cent. of alumina.[2] Aluminium is present also in the solar atmosphere.

326 *Preparation of Metallic Aluminium.*—The process which Wöhler used for the preparation of aluminium is one which may be employed for the preparation of all those elements which occur in nature combined with oxygen, and whose oxides are not reducible either in the presence of carbon or of hydrogen. It consisted[3] in fusing together potassium and chloride of aluminium in a closed crucible. The metal was thus obtained in the form of a grey powder, which, under the burnisher, exhibited a

[1] Yoshida, *Journ. Chem. Soc.*, 1887, **51**, 748; Berthelot and Andrée, *Compt. rend.*, 1895, **120**, 288; see also Smith, *Chem. News*, 1903, **88**, 135.

[2] Aderholdt, *Annalen*, 1852, **82**, 111.

[3] *Pogg. Ann.*, 1827, **11**, 146.

metallic lustre, and when pressed in an agate mortar adhered together in the form of glittering particles.

Wöhler afterwards improved his method, and, by passing the vapour of aluminium chloride over potassium, obtained the metal in fused globules.[1] In the year 1854 Bunsen [2] prepared aluminium by electrolysis of the chloride, and in the same year Deville commenced his first experiments on the preparation of aluminium on a large scale. The process he employed was that of Wöhler, potassium being, however, replaced by sodium, and he found that instead of the pure chloride it was preferable to use the double chloride of aluminium and sodium. In the Paris Exhibition of 1855 the "silver made from clay" naturally attracted great attention. Deville then, in concert with other chemists, and with the pecuniary help of Napoleon III., extended his experiments; with their help the process was still further improved, and alumimium was first prepared on the large scale at works near Alais, under the direction of Merle.

Pure aluminium hydroxide (p. 720) was made into balls with common salt and coal dust, and the mixture exposed at a white heat to a current of chlorine, by the action of which the volatile double chloride of sodium and aluminium, $NaCl,AlCl_3$, was produced. The latter was then heated with metallic sodium and a flux, and the aluminium run into moulds.

Electrolytic Production of Aluminium.—The above method for the preparation of the metal has now, however, been entirely superseded by an electrolytic process. Instead of electrolysing fused sodium aluminium chloride, a fused mixture of cryolite and common salt was substituted for the chloride by Bernard Bros., of Paris, who from 1887 manufactured the metal in this manner. In America the brothers Cowles succeeded in producing aluminium bronze by acting on alumina with carbon at the temperature of the electric furnace in the presence of metallic copper, but this method has now been replaced by more modern electrolytic processes. There are two processes employed, which differ only in detail:—the Hall process used in the United States, and the Héroult process employed by the British Aluminium Co. and in Europe. Pure aluminium oxide is dissolved in a bath of fused cryolite and electrolysed with carbon anodes. The walls of the box containing the electrolyte, which is of iron lined with carbon, act as the cathode. When the electrolysis has proceeded for a short time the molten

[1] *Annalen*, 1836, **17**, 44; 1841, **53**, 422. [2] *Pogg. Ann.*, 1854, **92**, 648.

aluminium acts as the cathode. In order to prevent loss of heat by radiation and to minimise the burning away of the electrodes, the top of the bath is covered with a layer of charcoal. From time to time the aluminium is tapped off and the bath renewed by the addition of fresh quantities of alumina. The cryolite simply acts as a solvent for the alumina and by proper regulation of the current takes no part in the electrolysis. Aluminium is deposited at the cathode and oxygen is liberated at the anode. The anodic oxygen unites with the carbon of the anode, forming carbon monoxide which burns to dioxide. For every pound of metal produced, from 0·5 to 0·7 lb. of anode is consumed. Several anodes are used in each bath and these take about 7,000 amperes at 7 volts. The anodes used by the British Aluminium Co. are about 10 inches square and are made from petroleum coke.

When possible, as at Foyers, Niagara, Neuhausen, Christianssand, &c., water power, as being cheaper than steam power, is utilised for the production of the necessary electric current. Alloys can also be made directly, instead of the metal itself, by carrying out the electrolysis in the presence of the desired metal, which dissolves the aluminium as it is liberated. Manufactured electrolytically, aluminium contains uniformly over 99 per cent. of metal and is very soft and ductile, the chief impurities being iron and silicon, and occasionally traces of sodium and copper.[1] When made by the sodium reduction process it usually contained only 97–98 per cent. of metal, and was more brittle and harder to work in consequence of the presence of larger amounts of silicon and iron; small amounts of sodium, nitrogen, and carbon were also usually present. A sample of commercial aluminium manufactured at Foyers, which contained 99·75 per cent. of the metal, was found by spectroscopic examination to contain sodium, potassium, calcium, copper, silver, gallium, iron, manganese, lead, and traces of indium. Silver, copper, and gallium were also found in the bauxite of Glenravel from which the aluminium was extracted.[2] The annual output of aluminium slowly increased between 1859 and 1888 from one ton to three tons, but from about the latter date the production rose very rapidly, and now reaches from 50,000 to 60,000 tons per annum, 250,000 to 300,000 h.p., with an

[1] Moissan, *Compt. rend.*, 1895, **121**, 794, 851; 1897, **125**, 276; Defacqz, *ibid.*, 1897, **125**, 1174.

[2] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 547.

additional large stand-by power, being employed in the industry.

Pure aluminium was prepared by Mallet [1] from a compound of aluminium bromide with the chlorides of potassium and sodium, by heating with sodium in a crucible lined with a mixture of alumina and sodium aluminate. The product was quite free from silicon, iron, sodium, and potassium.

327 *Properties.*—Aluminium is a tin-white metal, which is capable of assuming a bright polish. The appearance of objects made of aluminium is, however, improved by giving to the surface of the metal a dead appearance. This is accomplished by acting on the surface with weak soda-lye, and afterwards washing with dilute nitric acid. Aluminium is malleable and can be drawn into fine wire and hammered into very thin leaf. It can be best worked at a temperature of 100° to 150°. In the compact state it is very sonorous, emitting a tone when struck like that of flint glass. The cast metal has a specific gravity of 2·56, and is as hard as silver, whilst the hammered metal has the hardness of soft iron, and a specific gravity of 2·67. The hardness is again diminished by further heating, and at 600° the metal can easily be broken and at a somewhat higher temperature can be crushed in a mortar.[2] It fuses at 654·5° (Heycock and Neville), 657·3° (Holborn and Day).[3] In order to re-melt the metal a fusing mixture of common salt and potassium chloride must be employed, as the presence of other fluxes, such as borax, glass, &c., renders the metal very impure.

On slowly cooling it assumes a crystalline structure, the forms indicating that it crystallises in octahedra. Its electrical conductivity is 31·7 times that of mercury, whilst its thermal conductivity is 37·3 per cent. of that of silver, and is therefore slightly greater than that of zinc. The specific heat of the metal is 0·214 (Hillebrand), 0·222 (Richards).[4] The tensile strength of aluminium in bars is 28,000 lbs. per square inch, whilst that of a high carbon cast steel is 132,000. Pure aluminium does not oxidise at ordinary temperatures on exposure to air, but the impure metal soon becomes covered with a thin coating of oxide. When heated in oxygen it oxidises only on

[1] *Phil. Trans.*, 1880, **171**, 1022.

[2] Granger, *Bull. Soc. chim.*, 1902, (3), **27**, 789.

[3] *Ann. Phys.*, 1900, (4), **2**, 505. See also Holman, Lawrence and Barr, *Phil. Mag.*, 1896, (5), **42**, 37.

[4] *Chem. News*, 1892, **65**, 97; see also Pionchon, *Compt. rend.*, 1892, **115**, 162.

the surface without combustion. If a fine aluminium wire be wound round a piece of charcoal, the metal burns brightly with the charcoal in oxygen, and if a piece of thin aluminium foil or leaf be heated in a glass globe in an atmosphere of oxygen, it burns with a sudden flash of intensely white light. Clean aluminium powder, however, burns completely in air if strongly heated at one point, a small amount of nitride being formed along with the oxide.[1] Aluminium foil or powder decomposes water at 100°, being slowly converted into the hydroxide which in the former case retains the form of the foil. It is not attacked at the ordinary temperature by water which has been boiled, but is acted on by ordinary water.[2] It precipitates the metals lead, silver, and zinc from alkaline solutions, whilst neutral or acid solutions are not altered by it. It also precipitates metallic copper from a solution of copper sulphate.

Hydrochloric acid is the best solvent for aluminium. Dilute sulphuric acid, however, also dissolves it slowly with evolution of hydrogen, and concentrated sulphuric acid dissolves it on heating with evolution of sulphur dioxide. Dilute nitric acid acts slowly on the metal in the cold, ammonium salts being produced, but exerts a fairly vigorous action at the boiling point. The action diminishes as the concentration of the acid increases.[3] Organic acids attack it only slightly, but it dissolves in them with ease if the protecting layer of hydrogen which is produced is mechanically removed.[4] Aluminium is dissolved by aqueous alkalis, including ammonia, hydrogen being evolved. It is attacked also by sodium carbonate, both hydrogen and carbon dioxide being evolved and sodium aluminate produced. Sodium chloride also attacks the metal slowly, its action being greatly accelerated by the presence of a weak acid such as acetic acid, which dissolves the hydroxide formed (Ditte). The action of such a mixture is, moreover, greatly, increased by exposure to the air. According to Wöhler aluminium foil takes fire in a current of chlorine, but according to Böttger this is the case only when it is tied round with

[1] Matignon, *Compt. rend.*, 1900, **130**, 1391.

[2] Donatti, *Zeit. angew. Chem.*, 1895, 141.

[3] Lunge and Schmidt, *Zeit. angew. Chem.*, 1892, 7; Stillman, *J. Amer. Chem. Soc.*, 1897, **19**, 711; Woy, *Zeit. öffentl. Chem.*, 1903, **9**, 158; Watson Smith, *J. Soc. Chem. Ind.*, 1904, **23**, 475. Compare van Deventer, *Chemisch Weekblad*, 1906, **4**, 69.

[4] Ditte, *Compt. rend.*, 1898, **127**, 919; 1899, **128**, 195, 793.

brass wire to which some Dutch metal is fastened. At high temperatures aluminium also combines with sulphur, selenium, tellurium, phosphorus, arsenic, and carbon,[1] and it forms characteristic alloys with many metals.

Aluminium also forms compounds with alcoholic radicals, such as aluminium methide, $Al(CH_3)_3$, and ethide, $Al(C_2H_5)_3$, both of which are liquids and are spontaneously inflammable in the air.

Aluminium possesses so many valuable properties, such, for instance, as its low specific gravity, fine lustre, unalterability in the air and in sulphuretted hydrogen, non-poisonous qualities, and ease of working, that a widespread application of the metal was made as soon as the cheaper processes of manufacture lowered the price. Whilst the metal was sold previous to 1886 at £3 per lb., it can now be purchased for £80–85 per ton (1913), and has been as low as £50 per ton.

Aluminium is largely used for the production of carbon-free metals, especially manganese and chromium, and for the generation of intense heat to be used locally for the welding of iron and steel rails, &c. These processes have been developed by Goldschmidt,[2] whose patented "Thermite" consists of a mixture of granulated aluminium and the oxide of another metal, in equivalent proportions, the ignition of which causes the reduction of the metallic oxide present, owing to the strong affinity of aluminium for oxygen:

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

The reaction can only be commenced at a high temperature, and for this reason an ignition powder is used, consisting of a mixture of aluminium with barium peroxide; this mixture can be ignited by means of a match, and yields sufficient heat to commence the thermite reaction.

The temperature resulting from the above reaction may reach 3,000° C., and hence the process can be made use of in welding iron and steel materials, such as tram-rails, &c. According to one method the hot alumina resulting from the interaction of the aluminium and ferric oxide is poured round the two portions of metal to be welded, which are clamped tightly together when they have become sufficiently hot; in a second method the molten iron formed is itself allowed to flow around the portions

[1] See Matignon, *Compt. rend.*, 1900, **130**, 1391.
[2] See *J. Soc. Chem. Ind.*, 1898, **17**, 543.

of the metal to be welded, the exceedingly hot metal effecting a junction of the two surfaces and simultaneously by its own solidification mechanically strengthening the joint.

Aluminium is now largely used for electric cables, for the manufacture of boiling pans for varnish and for heating oils and melting waxes, for condenser tubes and also for cooking utensils. The pipes for conveying the nitrous fumes at the Atmospheric Nitric Acid works at Nottoden are also made of this metal.

Aluminium is also employed as a constituent of certain explosives, since it raises the temperature of explosion; thus *ammonal* consists of 72 per cent. ammonium nitrate, 3 per cent. carbon, and 25 per cent. aluminium.[1]

328 *Alloys of Aluminium.*—Copper forms alloys with aluminium possessing the colour of gold and very many of these are in use.[2] That containing about 10 per cent. of the latter metal is usually known as aluminium bronze and possesses the appearance of standard gold. For the preparation of this alloy chemically pure copper must be employed, as that which contains iron yields an inferior product. The alloy is malleable, yields fine castings, takes a high polish, and has a tensile strength almost equal to that of cast steel. It is now used for the manufacture of physical apparatus as well as of ornamental goods. Aluminium can be alloyed with silver, yielding a hard, easily polished alloy. That containing 4 per cent. of silver has been employed for the construction of beams for chemical balances, on account of its lightness and its unalterability in the air. Aluminium is also added to steel during casting, as it tends to prevent the formation of blow-holes on solidification, acting in a similar manner to silicon.

Gold and aluminium form a very interesting series of alloys. Gold containing 1 per cent. of aluminium has a green colour; with 10 per cent. it is white and brittle; and with 22 per cent. deep purple, this latter alloy having a melting point about 20° higher than that of pure gold.[3]

Aluminium combines easily with sodium and potassium, and the alloy containing only 2 per cent of sodium decomposes water.

Alloys of aluminium can be prepared in the way already

[1] Bichel, *Zeit. angew. Chem.*, 1905, **18**, 1889.

[2] Dagger, *J. Soc. Chem. Ind.*, 1894, **13**, 4.

[3] Roberts-Austen, *Proc. Roy. Soc.*, 1892, **50**, 367. Compare Heycock and Neville, *Phil. Trans.*, 1900, *A.*, **194**, 201,

described, and in many cases by adding the oxides, sulphides, or chlorides of the metals to molten aluminium, which reduces the added compound and forms an alloy with its metal.

Aluminium also combines with mercury when it is moistened with caustic alkali, or when the two metals are fused together in an indifferent gas. The amalgam is very brittle, oxidises easily in the air, and decomposes water at the ordinary temperature. The amalgam is also formed when aluminium foil is immersed in a solution of mercuric chloride. It has been employed as a reducing agent [1] for the estimation of nitrates in water and for the preparation of many organic compounds.

The following are the most important alloys of aluminium with their technical names:

Gold Bronze	Copper with 3 to 5% Al
Steel „	Cu 90·5, Al 8·5, Si 1·0
Steel „ (Brand P. B.)	Cu 89·5 Al 8·5, Si 2·0
Acid „ (Brand C.)	for cocks. Cu 90, Al 10
Hercules Metal	Cu 61·0, Al 1·5, Zn 37·5
Aluman	Brass with aluminium.
Argentan	Cu 70·0, Ni 23, Al 7
Magnalium	Aluminium and Magnesium.
Wolframinium	Al 97·7, Cu 0·4 Sn 0·1, Sb 1·4, W 0·4.

COMPOUNDS OF ALUMINIUM.

Aluminium and Oxygen.

329 Aluminium and oxygen form the stable oxide, Al_2O_3, which corresponds with the aluminium salts. There is also some evidence of the existence of one or more *lower oxides*, formed by the incomplete oxidation of aluminium in the air, or by the reduction of alumina by metallic aluminium.[2]

Aluminium Oxide or *Alumina*, Al_2O_3, is found in nature as the mineral corundum, which crystallises in hexagonal prisms, and occurs in several varieties. The more or less colourless crystals, as well as those which are coloured brown by ferric

[1] Ormandy and Cohen, *Journ. Chem. Soc.*, 1890, **57**, 811; Wislicenus, *J. pr. Chem.*, 1896, **54**, 18.

[2] Pionchon, *Compt. rend.*, 1893, **117**, 328; Duboin, *ibid.*, 1901, **132**, 826; Kohn-Abrest, *Bull. Soc. chim.*, 1904, (3), **31**, 232; *Compt. rend.*, 1905, **141**, 323.

oxide and which are either translucent or opaque, are called corundum: those which are coloured red by chromium compounds are termed ruby, whilst those which have a blue tint, due probably to cobalt, chromium, or an oxide of titanium, are known as sapphires. The yellow crystals are termed oriental topaz, and the purple oriental amethyst, whilst the green are called oriental emeralds. Coarse and granular corundum containing magnetite or hæmatite intimately mixed with it, and having a grey or blackish colour, is termed emery. Of this mineral there are many gradations, from the finely ground emery to those kinds in which the corundum is present in distinct crystals. Crystallised alumina is excelled in hardness only by the diamond and silicon carbide (carborundum), and hence it is largely used for polishing and grinding the surfaces of glass and metal.

When aluminium hydroxide or aluminium salts containing volatile oxyacids are heated, alumina remains either as a white powder or in amorphous gum-like masses. If this is not too strongly ignited it dissolves in concentrated acids, which, however, do not attack the crystallised compound. When more strongly ignited, amorphous alumina becomes denser and harder. After ignition in the flame of the spirit lamp it has a specific gravity of 3·5, and when more strongly heated in a porcelain-kiln it attains a specific gravity of 3·9. It is then nearly as hard as corundum but still amorphous (H. Rose). Alumina melts at 1,880° to a thin liquid, which, on cooling, assumes a crystalline structure and possesses all the properties of corundum. A similar oxide may be obtained by the combustion of the finely divided metal. If aluminium hydroxide is moistened with potassium dichromate and the dried mass fused before the oxy-hydrogen blow pipe, artificial ruby is obtained (Gaudin), and the same material may be prepared by heating to whiteness a mixture of borax and amorphous alumina containing a small quantity of chromium sesquioxide (Ebelmen). Crystallised alumina is also obtained when aluminium fluoride is allowed to act upon boron trioxide at a very high temperature (Deville and Caron), when aluminium phosphate is fused with sodium sulphate (Debray), and when alumina is heated to dull redness in hydrochloric acid gas at a pressure of three atmospheres.[1]

Fremy and Feil [2] obtained crystallised alumina on the large

[1] Hautefeuille and Peney, *Compt. rend.*, 1890, **110**, 1038.
[2] *Compt. rend.*, 1877, **85**, 1029.

scale by heating equal parts of alumina and lead oxide to a bright red-heat. The product consisted of two distinct layers: one of these was composed of lead silicate derived from the action of the lead oxide upon the silica of the crucible; the other was a vitreous mass, and contained cavities filled with colourless crystals of corundum. By the addition of from 2 to 3 per cent. of potassium dichromate to the materials crystals of ruby were obtained, whilst crystals of sapphire were prepared by adding a trace of oxide of cobalt. Splendid crystals of rose-red coloured ruby were obtained by heating a mixture of equal parts of alumina and barium fluoride with from 2 to 3 per cent. of potassium dichromate to a very high temperature in a glass furnace. This is explained by the production of a volatile fluoride of aluminium which undergoes decomposition in contact with the gases of the furnace, with evolution of hydrofluoric acid and deposition of crystalline alumina, the crystals being found in the upper part of the crucible. Similar rose-red crystals are formed when chlorine is passed over a heated mixture of sodium aluminate and 1 per cent. of potassium dichromate.[1]

In order to dissolve crystallised alumina it must either be fused with caustic potash or with acid potassium sulphate. It is also dissolved when heated in sealed tubes with concentrated sulphuric acid.

Hydroxides of Aluminium.—Several of these occur in nature. The most important are hydrargillite or gibbsite, $Al(OH)_3$; diaspore, $AlO(OH)$, both of which are crystalline; and bauxite, impure Al_2O_3, which is found as an amorphous mass of varying composition.

When ammonia is added to a soluble salt of aluminium in the cold, a gelatinous precipitate falls down, but when it is added at the boiling point an opaque white precipitate is deposited.

The composition of the amorphous hydroxide thus obtained is a matter of some doubt. According to Ramsay,[2] when dried in the air it has the composition $Al_2O_3,5H_2O$ and gradually loses water as the temperature is raised, until at 300° it has approximately the composition Al_2O_3,H_2O. Allen,[3] on the other hand, considers that the amorphous hydroxide is $Al(OH)_3$ or $Al_2O_3,3H_2O$; when it is heated at 100° or dried over sulphuric acid it forms $Al_2O_3,2H_2O$, which is hygroscopic and takes up water again from the air, regaining its original composition.

[1] Loyer, *Bull. Soc. chim.*, 1897, [3], **17**, 345.

[2] *Journ. Chem. Soc.*, 1877, ii., 395.

[3] *Chem. News*, 1900, **82**, 75.

The freshly precipitated hydroxide is easily soluble in acids, but the naturally occurring crystallised hydroxides are attacked by acids only after moderate heating. The ordinary hydroxide, however, when preserved under water for several months becomes very difficultly soluble in alkalis and acids, with the exception of concentrated sulphuric acid, in which it dissolves readily. This form of hydroxide has the composition $Al_2O_3,3H_2O$ and is termed by Tommasi [1] the δ-modification.

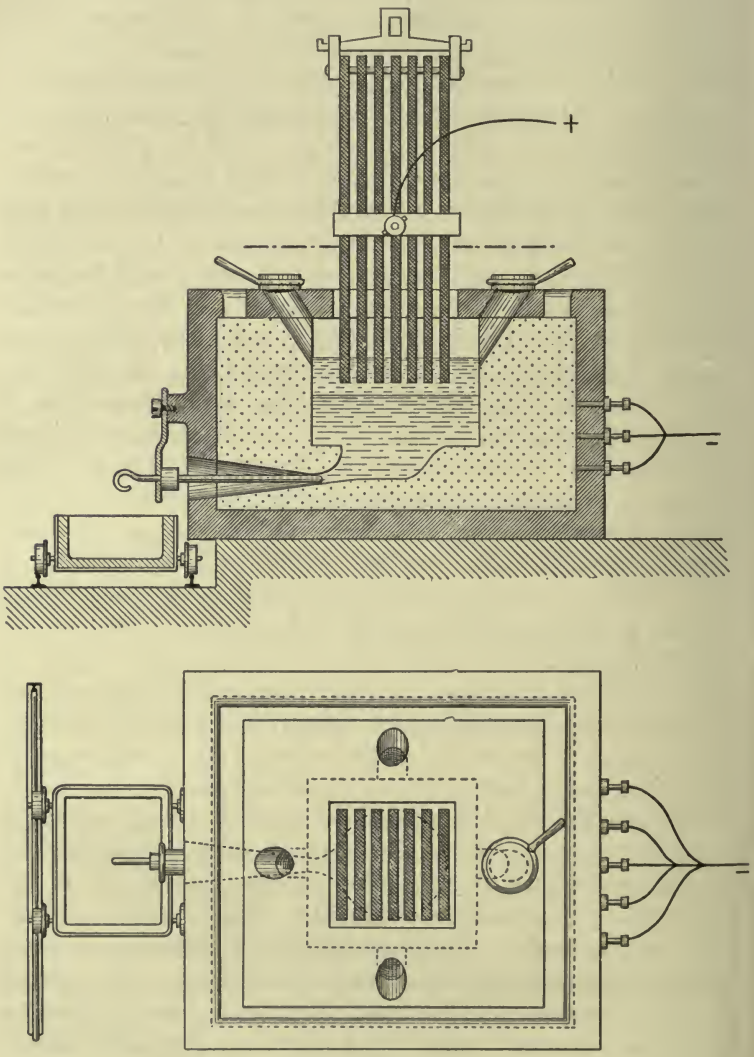
The amorphous hydroxide is also readily soluble in caustic alkalis, and appears to form a salt of the type M^IAlO_2. This salt, however, is rapidly hydrolysed with formation of the free alkali and production of free aluminium hydroxide, which at first appears to remain dissolved in the colloidal form [2] and then separates out gradually as a precipitate which is much less soluble, both in acids and alkalis, than the original hydroxide. This precipitated hydroxide is generally regarded as being identical with the crystalline mineral gibbsite,[3] but according to Russ [4] it is not crystalline and is best known as the β-modification. The amount of precipitate obtained depends on the temperature, the concentration and the molecular ratio of soda and alumina present. Thus at 21°, with a solution containing $Al_2O_3 : Na_2O = 1 : 1{\cdot}24$, the maximum yield is obtained from a solution of specific gravity 1·173 and amounts to 86% of the alumina present.

This reaction is utilised in the preparation of aluminium hydroxide from bauxite, which is carried out on a very large scale to provide material for the manufacture both of metallic aluminium and of many of the salts. The alumina is made from native bauxite, which contains ferric oxide, silica, and small quantities of titanic oxide. In order to remove these impurities the bauxite is roasted to oxidise the iron completely to the ferric state. It is then digested under pressure of about 80 lbs. with caustic soda. Sodium aluminate is thus formed from which the impurities are filtered off after dilution. The solution of sodium aluminate is then treated with some pure precipitated aluminium hydroxide, when the bulk of the aluminium is precipitated as Al_2O_3, which after washing and drying is obtained

[1] *Journ. Chem. Soc.* 1905, **88**, ii., 712.
[2] Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 296
[3] Ditte, *Compt. rend.*, 1893, **116**, 183.
[4] Russ, *Zeit. anorg. Chem.*, 1904, **41**, 216.

as a snow white powder. The alkali solution is concentrated and employed again.

As the process of obtaining Al_2O_3 is rather expensive,



FIGS. 175, 176.

many attempts have been made to manufacture aluminium from other aluminium compounds, but hitherto unsuccessfully. Figs. 175 and 176 represent the Hêroult furnaces. The hydr-

oxide is also manufactured from cryolite by the process already described under the alkali manufacture (p. 303).

Aluminium hydroxide as usually obtained is only very slightly soluble in aqueous ammonia, but a form soluble in ammonia can be prepared by the decomposition of certain aluminates with ammonium chloride and a large excess of ammonia. The hydroxide readily dissolves in methylamine and other organic bases.[1]

Aluminium hydroxide occurs also in two soluble modifications, both of which are colloidal. One of these, which when dried at 100° has the composition $Al_2O(OH)_4 = Al_2O_3 + 2H_2O$, was obtained by Walter Crum[2] by preparing a solution of normal aluminium acetate by the mutual decomposition of lead acetate and aluminium sulphate. This, on heating, decomposes with separation of the basic acetate, $Al_2(C_2H_3O_2)_4(OH)_2,H_2O$, which becomes soluble on treatment for one and a half hours with 200 times its weight of boiling water. If this solution is allowed to stand for ten days and nights at the temperature of boiling water in a closed flask, the acetic acid separates from the alumina. After a sufficient quantity of water has been added to reduce the percentage of alumina to 0·25, the liquid is heated in a flat basin to the boiling point, fresh water being constantly added to replace that lost by evaporation, until all the acetic acid has been driven off. The solution then is perfectly neutral and tasteless, but becomes gelatinous on evaporation.

The second soluble hydroxide of aluminium was obtained by Graham[3] by dialysis of the basic chloride obtained by dissolving the hydroxide in the normal chloride. The normal salt passes through the parchment paper into the water, and a neutral tasteless solution containing alumina remains in the dialyser. This is very unstable, and after some days passes into a jelly. Both these soluble hydroxides are coagulated on the addition of traces of a salt, an acid, or an alkali. Graham's compound acts as a mordant, uniting with colouring matters to form lakes, and in the coagulated state is readily soluble in acids. Crum's compound, on the other hand, termed by Graham "meta-aluminium hydroxide," does not combine with colouring matter and does not dissolve in excess of acid.

Precipitated aluminium hydroxide possesses in high degree

[1] Renz, *Ber.*, 1903, **36**, 2751.

[2] *Chem. Soc. Quart. Journ.*, 1854, **6**, 216.

[3] *Phil. Trans.*, 1861, **151**, 183. See also Schneider, *Annalen*, 1890, **257**, 359; Hantzsch and Desch, *Annalen*, 1902, **323**, 30.

the power of withdrawing from solution both inorganic salts and organic bodies. This property is employed in dyeing.

Aluminium peroxide,[1] $Al_2O_3,Al_2O_4,10H_2O$, is obtained by adding an excess of 30 per cent. hydrogen peroxide to aluminium hydroxide dissolved in 30 per cent. solution of potassium hydroxide. Probably the first product of the reaction is Al_2O_4, which is changed by hydrolysis.

Aluminates.—Like other weak bases, alumina acts toward the stronger bases as an acid-forming oxide; thus precipitated alumina dissolves in solutions of the caustic alkalis forming definite salts, which can also be prepared by the action of the alkalis on metallic aluminium.[2]

Potassium Aluminate, $KAlO_2,1\frac{1}{2}H_2O$, is obtained in hard glistening crystals when alumina and potash are fused together in a silver basin, the solid residue dissolved in water, and the solution evaporated in a vacuum.

Sodium Aluminate, $NaAlO_2$.—This substance has not been obtained in the crystalline state. It is prepared on the large scale by fusing cryolite with lime, or bauxite with soda or sodium sulphate and carbon, as well as with common salt in a current of steam. When the melted mass is lixiviated with water and the solution evaporated to dryness, sodium aluminate is obtained. As already mentioned, its aqueous solution decomposes in presence of aluminium hydroxide. This substance is used as a mordant in dyeing and calico-printing, for the preparation of coloured lakes and of pure alumina, and for the sizing of paper, &c.

Calcium Aluminate, $CaAl_2O_4$, is formed in colourless transparent needles of sp. gr. 3·671 at 20° when ignited alumina is heated with lime in the electric furnace. It does not belong to the group of the spinels.

Magnesium Aluminate, $MgAl_2O_4$.—This substance occurs in nature as spinel. It crystallises in the rhombic system, and is either colourless or variously tinted, and is classed in various species according as either the whole or a part of the magnesium and aluminium is replaced by isomorphous metals. Thus spinel is $(Mg,Fe)(Al,Fe)_2O_4$; zinc-spinel or gahnite is $(Zn,Fe,Mg)(Al,Fe)_2O_4$, &c.

The naturally occurring aluminates were artificially prepared by Ebelmen, by fusing alumina and the corresponding oxide

[1] Terni, *Atti R. Accad. Lincei*, 1912, [v.], **21**, ii., 104.

[2] See Allen and Rogers, *Amer. Chem. J.*, 1900, **24**, 304.

with boron trioxide. This latter substance, which served as a solvent, was almost entirely volatilised at a very high temperature. In this way colourless spinel was obtained, and this was coloured red by chromium, blue by cobalt, and black by iron; by a similar process the aluminates of barium, glucinum, iron, manganese, &c., can be prepared. Deville and Caron also obtained crystals of gahnite and chrysoberyl by heating aluminium fluoride, together with fluoride of zinc or glucinum, in a carbon crucible which contained a platinum basin filled with boron trioxide.

Salts of Aluminium.

330 Aluminium forms only one series of salts, in which one atom of the metal replaces three atoms of hydrogen. Alumina acts as a very weak base and the salts, especially those derived from weak acids, such as acetic acid, are very readily decomposed by boiling their aqueous solutions, a basic salt or the hydroxide being formed.

Many compounds of aluminium are isomorphous with the corresponding compounds of iron, manganese and chromium.

Aluminium and the Halogens.

331 *Aluminium Fluoride*, AlF_3, is best obtained by evaporating to dryness a solution of aluminium in hydrofluoric acid, and subliming the residue, contained in a carbon tube, in a current of hydrogen.[1] It forms transparent, very obtuse rhombohedra, which were formerly supposed to be cubes. It is permanent in the air, insoluble in water, and unaltered in the presence of acids and aqueous alkalis, but it is decomposed by long-continued fusion with sodium carbonate. Aluminium dissolves readily in excess of hydrofluoric acid, and from this solution the hydrate $2AlF_3,7H_2O$ can be obtained in two forms, one soluble and the other insoluble in water.[2] The fluoride forms a series of double fluorides, of which the most important is:

Aluminium Sodium Fluoride, $AlF_3,3NaF$.—This occurs as the mineral cryolite at Evigtok, in the Arksutfjord, on the west coast of Greenland, where it forms a bed 80 feet thick and 300 feet long. It was discovered in this locality by Andrada

[1] Brunner, *Pogg. Ann.*, 1856, **98**, 488.
[2] Baud, *Compt. rend.*, 1902, **135**, 1103.

at the end of the eighteenth century. Its mineralogical name was given to it by him inasmuch as it had an ice-like appearance. The investigations of Albidgaard showed that it contained hydrofluoric acid, alumina, and an alkali metal, and Klaproth found the alkali to be soda. The exact composition of cryolite was determined by Vauquelin, Berzelius, and Deville, and in 1849–1850 Julius Thomsen showed that this mineral could be decomposed in the dry way by means of lime and lime salts as well as in the wet way, and upon this observation an important Danish industry was founded (p. 303). Cryolite usually occurs in masses of a snow-white, reddish, brownish, or bluish colour, which possess easy cleavage; it is found more rarely in triclinic crystals. When acted upon with concentrated sulphuric acid it evolves hydrofluoric acid, and the residue contains sodium sulphate, which may be dissolved by the action of cold water, the anhydrous aluminium sulphate, which is formed at the same time, dissolving only in boiling water.

Aluminium Chloride, $AlCl_3$, was first prepared by Oersted by heating a mixture of carbon and alumina in a current of dry chlorine. This method was afterwards adopted and improved by Wöhler,[1] Liebig,[2] Bunsen,[3] and Deville.[4] On the large scale it is prepared in an apparatus similar to that formerly used for the production of the double chloride of aluminium and sodium. It may also be readily prepared in a pure condition by heating aluminium in chlorine or in hydrochloric acid gas,[5] the reaction, in the latter case, proceeding when once started without requiring any external heating.[6]

Pure aluminium chloride is a white crystalline solid. It usually possesses, however, a yellowish or greenish colour, due to the presence of ferric chloride and other impurities. When heated it volatilises slowly without fusion, and condenses in hexagonal tablets, but if a large quantity is quickly heated the mass fuses and then boils. When heated in a sealed tube it melts at 194°; the boiling point of the liquid appears to be somewhat below 179°.[7] The specific gravity of the vapour, according to the experiments of Nilson and Pettersson (p. 33),

[1] *Pogg. Ann.*, 1827, **11**, 146.
[2] *Pogg. Ann.*, 1830, **18**, 43.
[3] *Pogg. Ann.*, 1854, **92**, 648.
[4] *Compt. rend.*, 1849, **29**, 321.
[5] Nilson and Pettersson, *Zeit. physikal. Chem.*, 1887, **1**, 459; Stockhausen and Gattermann, *Ber.*, 1892, **25**, 3521; Gustavson, *J. pr. Chem.*, 1901, (2), **63**, 110.
[6] Escales, *Ber.*, 1897, **30**, 1314.
[7] Seubert and Pollard, *Ber.*, 1891, **24**, 2575.

corresponds to the formula $AlCl_3$ at temperatures above 750.°[1] The molecular weight of the chloride in solution in pyridine,[2] as determined by the boiling point method, also corresponds with the formula $AlCl_3$. Aluminium chloride is hygroscopic, absorbing water from the air and emitting fumes of hydrogen chloride. It is also easily soluble in alcohol and ether.

When hydrochloric acid gas is passed into a solution of aluminium chloride in concentrated hydrochloric acid, large hexagonal prisms having the composition $AlCl_3,6H_2O$ separate out;[3] these are obtained also by the evaporation of a solution of aluminium chloride in water or of aluminium hydroxide in hydrochloric acid, and on further heating are easily decomposed into water, hydrochloric acid, and residual alumina.

Aluminium chloride absorbs dry ammonia gas and yields a bulky white powder of the composition $AlCl_3,6NH_3$, which loses one molecule of ammonia at 180°, and when heated in a stream of hydrogen at 450° yields a sublimate of the compound $AlCl_3,NH_3$. At −23° a compound, $AlCl_3,9NH_3$, is produced.[4] The compound, $AlCl_3,3NH_3$, described by Persoz, appears not to exist. Aluminium chloride also combines with phosphorus pentachloride, phosphorus oxychloride, carbonyl chloride, sulphuretted hydrogen,[5] sulphur dioxide, sulphur tetrachloride,[6] the chlorides of silver, selenium, and tellurium, as well as with other metallic chlorides. It is largely employed for the synthesis of organic compounds.

Sodium Aluminium Chloride, $AlCl_3,NaCl$.—The preparation of this compound on the large scale has already been described. It is obtained as a colourless crystalline mass which melts at 185° (Bunsen) and volatilises at a red-heat. It readily absorbs water, but in the compact state it is less hygroscopic than aluminium chloride, and for this reason it was used instead of the latter compound in the preparation of aluminium.

Aluminium Bromide, $AlBr_3$.—When aluminium and bromine are brought together they combine with evolution of heat, form-

[1] *Zeit. physikal. Chem.*, 1887, **1**, 459; 1889, **4**, 206.

[2] Werner, *Zeit. anorg. Chem.*, 1897, **15**, 1. Compare Kohler, *Amer. Chem. J.*, 1900, **24**, 385.

[3] Dennis, *Zeit. anorg. Chem.*, 1895, **9**, 339.

[4] Baud, *Compt. rend.*, 1901, **132**, 134, 690. Compare Stillman and Yoder, *Amer. Chem. J.*, 1895, **17**, 748; and Persoz, *Ann. Chim. Phys.*, 1830, [2], **44**, 319.

[5] Baud, *Compt. rend.*, 1902, **134**, 1429; 1905, **140**, 1688.

[6] Ruff, *Ber.*, 1901, **34**, 1749; 1902, **35**, 4453.

ing the above compound. It is obtained by passing the vapour of bromine over the metal or a heated mixture of alumina and carbon. It forms pale yellow rhombohedral crystals[1] which melt at about 90°, boil at a temperature between 265° and 270° and sublime in crystalline scales. The specific gravity of the solid is 2·54. In other respects it is analogous to the chloride, and forms the hydrate $AlBr_3,6H_2O$, which is obtained also by dissolving aluminium hydroxide in hydrobromic acid and carefully evaporating the solution. The molecular weight as determined by the boiling point and freezing point methods with a solution of the bromide in bromine,[2] and by the boiling point method with a solution in carbon disulphide,[3] corresponds with the formula Al_2Br_6. The bromide forms a conducting solution in ethyl bromide, from which aluminium may be deposited by electrolysis.[4]

Aluminium Iodide, AlI_3, is formed when the metal and iodine are heated together in closed tubes, or brought together in presence of carbon disulphide. It is deposited in colourless crystals which melt at 185° (Weber) and boil at a temperature of 360°. Its specific gravity is 2·63. The vapour is combustible, giving rise to an explosive mixture when diluted with air. It is soluble in water, alcohol, and carbon disulphide, and forms a crystalline hydrate, $AlI_3,6H_2O$. Aluminium iodide has been employed for the purpose of converting organic chlorine compounds into iodides. Thus carbon tetrachloride yields the corresponding tetraiodide when heated with aluminium iodide (Gustavson):

$$4AlI_3 + 3CCl_4 = 4AlCl_3 + 3CI_4.$$

Aluminium and the Elements of the Sulphur Group.

332 *Aluminium Sulphide*, Al_2S_3.—Aluminium combines with sulphur at a red-heat to produce this compound,[5] which is a yellow mass. It is also formed when sulphur is added to a strongly heated mixture of alumina and charcoal,[6] when the vapour of carbon disulphide is passed over strongly heated alumina and,

[1] Patten, *J. Physical Chem.*, 1904, **8**, 548.
[2] Beckmann, *Zeit. anorg. Chem.*, 1906, **51**, 96
[3] Kohler, *Amer. Chem. J.*, 1900, **24**, 385.
[4] Poltnikoff, *J. Russ. Phys Chem. Soc.*, 1902, **34**, 466; Patten, *J. Physical Chem.*, 1904, **8**, 548.
[5] Knapp and Ebell, *Dingl. Polyt. Journ.*, 1878, **229**, 69, 173.
[6] Bucherer, *Zeit. angew. Chem.*, 1892, 483.

along with oxysulphide, when sulphuretted hydrogen is passed over heated alumina.[1] It becomes crystalline when heated in the electric furnace.[2]

It is decomposed by water with formation of sulphuretted hydrogen and aluminium hydroxide. The *selenide*[3] and *telluride*[4] are also formed by direct union of the elements.

Aluminium Sulphate, $Al_2(SO_4)_3$, is obtained by dissolving the hydroxide in dilute sulphuric acid. It crystallises with difficulty, forming pearly six-sided monoclinic tablets containing $18H_2O$. It possesses a sweet astringent taste, and dissolves in two parts of cold water, scarcely at all in alcohol (Berzelius), and readily in glycol. This hydrated salt is found as the mineral keramohalite in the neighbourhood of active volcanoes, and in alum shale. It melts on heating in its water of crystallisation, and then swells up, the anhydrous compound being left behind as a porous mass, dissolving only slowly again in water. At a red-heat it is decomposed, leaving a residue of pure alumina. The concentated solution of this salt is a useful reagent for potassium salts, as potassium alum, $Al_2K_2(SO_4)_4,24H_2O$, is precipitated as a crystalline powder, which is almost completely insoluble in an excess of aluminium sulphate.[5] A hydrate with $9H_2O$ is precipitated from aqueous solutions of the sulphate by alcohol, and a hydrate with $6H_2O$ is formed when $Al_2(SO_4)_3,18H_2O$, is heated with concentrated sulphuric acid.[6]

Aluminium sulphate is prepared on the large scale, and is known in commerce under the name of concentrated alum or sulphate of alumina. For this preparation china clay, as free as possible from iron, is employed. This is roasted in a reverberatory furnace, by which any iron which may be present is rendered insoluble, whilst the aluminium silicate becomes more soluble in sulphuric acid. It is then heated in leaden boilers with sulphuric acid of specific gravity 1·45, and the solution is allowed to deposit the silica and any undecomposed alumina. The clear liquid is then evaporated down until a small portion on cooling is found to solidify. After cooling, the soft mass is cut into square blocks and thus brought into the market. This material is employed by the dyer as a mordant,

[1] Gautier, *Compt. rend.*, 1906, **143**, 7.
[2] Mourlot, *Compt. rend.*, 1896, **123**, 54.
[3] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314.
[4] Whitehead, *J. Amer. Chem. Soc.*, 1895, **17**, 849.
[5] Wurtz, *Dict.* i., 174. [6] Schmatolla, *Zeit. angew. Chem.*, 1903, **16**, 202.

and also for the purpose of weighting paper and for the treatment of sewage.

An impure product, known under the name of *alum-cake*, also used largely by paper-makers, is obtained by heating a white china clay or bauxite with sulphuric acid. The whole mass then becomes solid. It consists of about 12–15 per cent. of soluble alumina as sulphate, together with silica and undecomposed aluminate.

For many purposes a sulphate perfectly free from iron is needed. This is prepared by dissolving the pure hydroxide in sulphuric acid, or by treating a solution of the crude sulphate with pyrolusite (Spence) or calcium ferrocyanide solution (Kynaston).

According to Berzelius a series of basic sulphates of aluminium exists, but these are probably mixtures. One of them occurs in clay deposits as the mineral aluminite or websterite. It forms an earthy mass, having the composition $Al_2(SO_4)(OH)_4,7H_2O$. The same salt is formed when aluminium sulphate is precipitated with a quantity of ammonia insufficient to throw down the whole of the alumina. When a concentrated solution of aluminium sulphate is boiled with the freshly precipitated hydroxide a thick solution is formed, and this, on standing for some months, deposits a crust of small needle-shaped crystals of a salt having the composition $Al_2(SO_4)_2(OH)_2,2Al_2(SO_4)(OH)_4,25H_2O$ (Rammelsberg).

A crystalline soluble basic sulphate, $Al_2O_3,2SO_3$, can be prepared by heating an excess of alumina with sulphuric acid under pressure, adding a little lime, evaporating the clear liquor and allowing to crystallise.[1]

A crystalline *chlorosulphate*, $AlSO_4Cl,6H_2O$, is formed when concentrated hydrochloric acid is added to a solution of the sulphate. It is at once decomposed by water.[2]

The Alums.

333 Aluminium sulphate forms with the sulphates of the alkali metals double salts, which crystallise in regular octahedra, and the potassium double salt, $Al_2(SO_4)_3,K_2SO_4,24H_2O$, has long been known under the name of *alum*. This name is,

[1] Spence, German Patent, 167419 (17/4/1903).

[2] Recoura, *Compt. rend.*, 1902, **135**, 736.

however, now used to designate a whole group of bodies. A number of substances with an astringent taste were known to the Greeks (*στυπτηρία*) and the Romans (alumen), and among these the naturally occurring aluminium sulphate and alum seem to have been included. We also find the name occurring in the writings of the Latin Geber, who speaks of an ice-alum, which is obtained from Roccha, and which he was able to purify by recrystallisation. The alchemists of the West described this salt as *alumen de rocca*, in order to distinguish it from the vitriols, and this name was afterwards erroneously translated by the French chemists, who termed pure alum *alun de roche*.

In the thirteenth century an alum factory, erected by Italians, existed near Smyrna. They obtained their alum by roasting alum-rock, lixiviating the product, and crystallising. In the fifteenth century the Genoese erected alum works on the island of Ischia, and at the same time the celebrated works at Tolfa, in the Papal States, were established. The so-called Roman alum, which was there prepared, was, up to recent times, considered to be the best, and the manufacture has been resuscitated, 10,000 tons of alum being made annually at Tolfa by a French company. The material from which the alum is manufactured in various places in Italy, as well as in Hungary, is the alum-rock, the chief constituent of which is the mineral alunite or alum-stone, which is itself a double compound of potassium sulphate and basic aluminium sulphate, possessing the formula $K_2SO_4,3Al_2(SO_4)(OH)_4$. The rock is a product of the action of steam and sulphur dioxide on trachyte, and consists chiefly of a mixture of quartz and alum-stone. This is mixed with fuel in heaps, or in a furnace similar to a lime-kiln, and the roasted mass exposed for some weeks to the air. It then falls to a soft material, which is lixiviated with hot water, and the clear liquid, on standing, is concentrated in copper pans, and allowed to crystallise in wooden vessels. The crystals have a slightly orange-red colour, a very characteristic property of Roman alum, due to the presence of very finely divided ferric oxide, which is mechanically mixed in the mass. On crystallising the alum from hot water this is left behind in the form of a reddish deposit.

Another method for preparing alum has long been known and is described by Agricola and Libavius. For this purpose shale is employed. This chiefly occurs in the Silurian and

Devonian formations, and contains finely divided iron pyrites, distributed through a mass of bituminous shale. The shale is heaped together and is either allowed to decompose slowly by exposure to the air, or it is roasted. In either case the pyrites is oxidised with formation of ferrous sulphate and free sulphuric acid, both of which act upon the clay, producing aluminium sulphate, which is then dissolved out with water. It was early known that the ley thus obtained did not crystallise until an alkali had been added to it. Both Agricola and Libavius state that it is customary to add decomposed urine to the ley, in order, as the latter author remarks, to separate out the vitriol which is contained in solution. The alum thus prepared must have been chiefly ammonia-alum. This conclusion is corroborated by Kunkel's remark, for we find that he states distinctly in his *Laboratorium Chymicum* that alum contains the volatile alkali. Instead of urine, potash was soon used, and Hoffmann, in 1722, explained why an alkali was added, and this explanation, namely, that the crude ley was unable to crystallise because it was too acid, and also because it contained a sulphurous impurity which had to be removed by the addition of alkali, was the one which was accepted as correct until the end of the eighteenth century. At that time, and even up to a later date, it was not generally admitted that an alkali formed an essential constituent of alum. Moreover, alum was often prepared without the addition of such an alkali, for in those days the existence of a potassium compound in a mineral such as alunite was not known. Bergman and Scheele, who were well aware that alum contained potash, considered it to be an impurity. Marggraf then showed that pure alumina and sulphuric acid formed an alum only when an alkali was added, and hence Lavoisier concluded that two bases were contained in alum, viz., the alumina and the fixed alkali. These views were, however, not generally accepted until 1797, when Chaptel and Vauquelin showed that potash was an essential constituent of alum ; the latter chemist, moreover, proved that this fixed alkali could be replaced by ammonia, and asserted that when aluminous minerals yielded an alum on treatment with sulphuric acid, it was a proof that these minerals contained potash.

The crude ley from the lixiviation of the burnt shale consists essentially of the sulphates of aluminium and iron. The solution is then evaporated down in order that the iron salt may be deposited, and the solution ultimately obtained, which

has a specific gravity of 1·4, contains aluminium sulphate, with a small quantity of ferric sulphate. In order to obtain alum from this solution a potassium salt is added, and as the double salt formed is sparingly soluble, it separates out at once from the concentrated solution. It is most economical to employ a mixture of potassium sulphate and chloride, in different proportions, to be determined according to the composition of the ley, in order to avoid loss of aluminium as aluminium chloride or of potassium as ferrous potassium sulphate if ferrous sulphate be present. The crude potassium chloride from Stassfurt is now usually employed as the source of the potash. This substance is dissolved in a small quantity of hot water, and the solution added to the crude ley, and alum-meal is then obtained by well stirring the mixture until it is cold. The small crystals of which the meal consists are washed with a small quantity of cold water, the first wash-water being allowed to run into the boiling-down pans, and the last wash-water being employed for washing the crude alum. The purified meal is then dissolved in boiling water or by means of a current of steam, and the solution is brought into large crystallising vats built of movable staves bound together with iron hoops. In these the alum is deposited in the large crystals in which it is usually found in commerce.

Until recent years the chief quantity of alum made in England has been ammonium alum, prepared according to Spence's method. In this process the black bituminous shale lying above the coal-measures is employed as the source of alumina. This is made into heaps about 1·5m. in height and slowly roasted. The mass, which when roasted has a light red colour and is brittle, is then brought into large covered pans, mixed with sulphuric acid diluted with washings obtained in the final stages of the process, and heated by means of steam coils placed in the pan, until the liquors contain only a small percentage of free acid. The impure solution of aluminium sulphate is then run into cooling tanks, on the way receiving a sufficient quantity of either ammonium or potassium sulphate to convert it into ammonium or potassium alum as required. It is then diluted with liquors from a later stage in the process and stirred until cold to obtain small crystals of alum meal, the liquor run off, and the mealy alum washed with liquors and a small quantity of water. This is then drained and brought into a funnel shaped vessel, where steam is allowed to blow

on it in such a manner that the whole of the steam is condensed and all the salt dissolved. In half an hour about four tons of alum meal can thus be dissolved. The solution is allowed to settle in lead-lined cisterns, and then brought into crystallising vats and allowed to remain in them for a week. The staves are then knocked away, and a cylindrical block of alum remains, which is allowed to stand another week. A hole is afterwards drilled into the bottom of the block, the mother-liquor allowed to run out, and the mass broken up. Each vat yields three tons of large crystals, which frequently possess an amethystine tint resembling alum containing much iron, although they contain less than 0·001 per cent. of that metal. This colour is probably due to exceedingly minute quantities of iron and chromium, and not to organic matter, as has been usually supposed.

Since the introduction of cheap potassium chloride from Stassfurt, ammonium alum is no longer so largely made in England, potassium sulphate being manufactured by the action of sulphuric acid upon the natural potassium chloride in an ordinary salt-cake furnace, and employed instead of ammonium sulphate.

Shale is no longer used in many works as a source of alum, bauxite being employed and submitted to a similar treatment.

334 *Potassium Alum,* $Al_2(SO_4)_3,K_2SO_4,24H_2O$, is found in nature in feathery or mealy crusts or masses, as an efflorescence on alum shale, and in volcanic districts, where it is formed by the action of sulphur dioxide and oxygen on trachyte and lava. In some places, as in the districts near Naples and in Sicily, alum is produced in sufficient quantity to render its manufacture possible, and a very pure alum is obtained from this source. Potash alum has a specific gravity of 1·724 (Kopp); it crystallises in transparent regular octahedra, which often exhibit the cube and dodecahedron faces; its solution possesses a sweet astringent taste, and has an acid reaction. 100 parts of water dissolve (Locke):[1]

At	0°	10°	20°	30°	40°	
$K_2Al_2(SO_4)_4,24H_2O$	5·65	7·6	11·4	16·6	23·8	parts

At	50°	60°	70°	80°	
$K_2Al_2(SO_4)_4,24H_2O$	36·4	57·4	110·5	321·3	parts.

[1] See *Amer. Chem. J.*, 1901, **26**, 174; *Phil. Trans.*, 1904, **203**, A. 214.

It is insoluble in alcohol. On exposure to the air the surface becomes opaque and white. This is not, however, due to a loss of water, but is caused by the absorption of ammonia and the formation of a basic sulphate. When a crystal of alum is placed over sulphuric acid or heated to 61°, it loses 18 molecules of water (Graham); at 92° it melts in its own water of crystallisation; it loses the whole of its water slowly at 100°, and quickly at a higher temperature, with formation of what is known as burnt alum. This forms a porous mass, which dissolves slowly but completely in water. When alumina is fused with hydrogen potassium sulphate, an anhydrous salt is obtained which crystallises in small six-sided crystals, and remains behind when the fused mass is treated with hot water.

Neutral and Basic Alums.—If an alkali is slowly added to an alum solution, a precipitate is thrown down which disappears on stirring, but after a further addition of the alkali it remains unaltered. The solution in which the precipitate just redissolves has a neutral reaction, and is termed in commerce neutral alum; it is employed in dyeing, as it readily gives up alumina to the colouring matter, and is free from iron, inasmuch as the alkali decomposes any iron sulphate which the liquid may contain. If this solution is allowed to evaporate at the ordinary temperature, a crystalline crust is deposited which contains the basic salt $Al_2(SO_4)_3,2Al(OH)_3$, together with potassium sulphate. If the solution is heated above 40°, common alum is formed, and a precipitate of $K_2SO_4,Al_2SO_4(OH)_4$ is thrown down, this latter substance being identical in composition with alunite from Tolfa. When a solution of basic alum is heated in sealed tubes to 230°, this compound is also obtained in crystals (Mitscherlich). Solutions which contain a small quantity of basic alum yield, on spontaneous evaporation, cubical crystals. These were first observed by Sieffert in 1772, and obtained by him by boiling alum with milk of lime. This so-called cubic alum has the same composition as common octahedral alum, and on heating the solution, to which a small quantity of alkali has been added, to a temperature above 100°, ordinary octahedral alum separates out. Roman alum obtained from alunite often occurs in commerce in cubical crystals.

Rubidium and cæsium also form alums which are very sparingly soluble,[1] and hence are employed, as has already been described, for the separation of these metals from potassium.

[1] See Locke, *Amer. Chem. J.*, 1901, **26**, 166.

Ammonium Alum, $Al_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$.—This salt is very similar to potassium alum. It has a specific gravity of 1·626, melts at 95°, loses water on heating, and, on ignition, leaves a residue of pure alumina. One hundred parts of water dissolve (Poggiale):

	At	0°	10°	20°	30°	
$Al_2(NH_4)_2(SO_4)_4,24H_2O$		3·9	9·5	15·1	22·0	parts.

	At	40°	50°	60°	
$Al_2(NH_4)_2(SO_4)_4,24H_2O$		30·9	44·1	66·7	parts.

Commercial alum frequently contains both potassium and ammonium in varying proportions.

A hydroxylamine alum is also known.

Sodium Alum, $Al_2(SO_4)_3,Na_2SO_4,24H_2O$.—It was formerly believed that aluminium sulphate did not form an alum with sodium sulphate, but this salt was prepared in the year 1816 by Zellner.[1] Sodium alum is much more readily soluble in water than the other alums. Its specific gravity is 1·6. It effloresces in the air, and loses the whole of its water at a temperature of from 40° to 50°, leaving an easily soluble residue. It is not manufactured on the large scale, as on account of its solubility it is difficult to prepare in the pure state.

Silver Alum, $Al_2(SO_4)_3,Ag_2SO_4,24H_2O$.—The isomorphism of many silver salts with the corresponding salts of sodium connects this metal closely with those of the alkalis, and silver likewise forms an alum. This is obtained by heating a mixture of silver sulphate and aluminium sulphate, together with some water, in sealed tubes, until the silver sulphate is dissolved. On cooling, octahedral crystals are deposited. These are, however, decomposed into their constituents by water.[2]

Besides the above-mentioned alums, a number of other alums are known in which the aluminium is replaced by isomorphous metals, such as iron, manganese, and chromium. A peculiar nomenclature has arisen in the description of these compounds. If none of the isomorphous metals replaces aluminium, as in the above-mentioned alums, each is an aluminium alum. The names, iron alum, chromium alum, and manganese alum, on the other hand, are used, as a rule, to designate the potassium double sulphates of these metals. If potassium is replaced

[1] See also Dumont, German Patent, 141670.

[2] Church and Northcote, *Chem. News*, 1864, **9**, 155.

by other metals, then the names of both metals must be mentioned, as, for instance, ammonium chromium alum, and so forth.

Selenic acid also forms a series of alums, having the general formula $M_2^{III}(SeO_4)_3,M_2^{I}SO_4,24H_2O$.

Aluminium sulphate also forms double salts with potassium and ammonium sulphates containing $8H_2O$, which are obtained by fusing the corresponding alums and maintaining the liquid at about 86°. Slender crystals of the new hydrates then separate, but they are difficult to prepare, and have not been carefully examined.[1] Their formation is of interest, because compounds of the same type are formed by the sulphates of thallium and the metals of the rare earths, which do not form true alums.

Aluminium and Nitrogen and Phosphorus.

335 *Aluminium Nitride*, AlN, is formed in small yellow crystals when aluminium is strongly heated in nitrogen.[2] It is rapidly decomposed by water. It is now being manufactured by the Société Générale des Nitrures in Savoy, by strongly heating bauxite with carbon and passing nitrogen gas over the mixture:

$$2Al_2O_3+3C_2+2N_2=4AlN+6CO.$$

The nitride is then treated with water and ammonia produced:

$$2AlN+3H_2O=Al_2O_3+2NH_3.$$

The alumina can be used for the manufacture of aluminium, or employed over again.[3]

Aluminium Nitrate, $Al(NO_3)_3$, is obtained by dissolving the hydroxide in nitric acid, and evaporating the solution with occasional addition of nitric acid. On cooling, the salt $Al(NO_3)_3,8H_2O$ separates out in very deliquescent prismatic needles. This salt decomposes at 150°, leaving a residue of pure alumina (Deville), and this reaction may be employed for the separation of aluminium from calcium and magnesium, metals whose nitrates do not decompose at so low a temperature. The solution of the normal nitrate is obtained by exactly precipitating

[1] Marino, *Gazz.*, 1905, **35**, ii., 341.
[2] Mallet, *Journ. Chem. Soc.*, 1876, ii, 349.
[3] Serpek, D.R.-P., 235213 and 236044; also 239909.

a solution of lead nitrate with aluminium sulphate. This solution is used as a mordant in calico-printing with alizarin colours.

Phosphides of Aluminium.—When a mixture of aluminium powder and red phosphorus is fired, the two elements unite, forming the compound AlP, which is decomposed by water with formation of aluminium hydroxide and phosphine.[1] Various other compounds, Al_5P_3,Al_3P_7 and Al_3P, have been described.[2]

Phosphates of Aluminium.—Normal *aluminium orthophosphate*, $AlPO_4$, is obtained as a gelatinous precipitate by adding a neutral solution of an aluminium salt to a solution of sodium phosphate. It is soluble in mineral alkalis and acids, and in ammonia.[3] If an acid solution of the salt be precipitated with ammonia, a basic salt, $3AlPO_4,5Al(OH)_3$, is thrown down: this, combined with nine molecules of water, forms the crystalline mineral wavellite. In addition to this, many other basic and double phosphates of aluminium occur in the mineral kingdom, of which the mineral turquoise or calaite, occurring in Persia and valued as a gem, is one of the most important. This is coloured a greenish or bluish colour by copper, and is the basic salt, $AlPO_4,Al(OH)_3,H_2O$. Most of the turquoise, not artificial, used in jewellery in former centuries as well as at the present time, and described in early works on mineralogy, is bone-turquoise or odontolite, a fossil bone or tooth coloured by phosphate of iron. An aluminium phosphate containing 38% of phosphoric oxide occurs in Algiers, at Fauzan and in the Island of Grand Connétable, and is employed as a source both of alumina and of phosphoric acid.[4]

Aluminium and Boron, Carbon, and Silicon.

336 The compounds of aluminium and boron have been described in Vol I., p. 716.

Aluminium Carbide, Al_4C_3, was obtained by Moissan by heating aluminium in a carbon crucible in the electric furnace,[5] and appears to be formed from the carbon monoxide produced.[6] It is also produced when alumina is heated with calcium carbide,

[1] Fonzes-Diacon, *Compt. rend.*, 1900, **130**, 1314.
[2] Franck, *Chem. Zeit.*, 1898, **22**, 236.
[3] See Caven and Hill, *J. Soc. Chem. Ind.*, 1897, **16**, 29.
[4] Grognot, *Rev. Gen. Chim.*, 1906, **9**, 149.
[5] *Compt. rend.*, 1895, **119**, 9. [6] Pring, *Journ. Chem. Soc.*, 1905, **87**, 1530.

and when aluminium is heated in carbon monoxide in presence of aluminium chloride.[1] It forms yellow crystals and is decomposed by water with formation of pure methane :

$$Al_4C_3 + 12H_2O = 4Al(OH)_3 + 3CH_4.$$

337 *Silicates of Aluminium.* It has already been stated that the various silicates of aluminium occur in combination with other silicates to form the chief constituents of the solid crust of the earth. The number of these compounds is extremely large, and only those can be mentioned in this work which possess a general interest.

Topaz, $Al_2SiO_4F_2$, occurs in granite, gneiss, and mica-schist in the form of rhombic prisms, which are transparent and usually colourless, or of a light- or dark-yellow colour. The finest topaz occurs in the Urals, Siberia, and Brazil. The common forms are not infrequently employed for the manufacture of polishing powder instead of emery.

Noble Garnet, $(Mg,Fe)_3Al_2Si_3O_{12}$.—This, like the other members of the group of garnets, crystallises in the regular system, the dodecahedron being the most prominent form. The crystals are transparent, and are coloured, according to the quantity of iron which they contain, from a pale yellow up to a dark red tint.

Potash Felspar or *Orthoclase*, $Al_3(Si_3O_8)_3K_3$, is mined in great quantity for the manufacture of porcelain and similar materials, and it has also been utilised as a source of potash by roasting with lime and then extracting with water; beyond selection at the mines of the cleavage fragments of the crystalline mineral, no artificial work is put upon the native product. Large quantities are shipped to the pottery districts of the Midlands, and before being used it is very finely ground, either alone or along with other materials. When strongly heated, felspar fuses, and on cooling does not again crystallise, but solidifies to a colourless glass; hence it is used either to act as a frit or fusible material to bind together most firmly the infusible particles of clay forming the body of the porcelain or earthenware, and so produce a hard, translucent, lustrous mass, or else to act as a flux on the surface of the porcelain or earthenware so as to give it a smooth glazed surface which it would not otherwise possess.

Hydrated Aluminium Silicate or *Kaolin*, $H_2Al_2Si_2O_8,H_2O$, is formed by the weathering of felspar, which loses the whole of its potash and two-thirds of its silica, and takes in their place

[1] Gunz and Masson, *Compt. rend.*, 1897, **124**, 187.

a small proportion of water. This substance is a distinct mineral species and frequently occurs crystallised in four- or six-sided tablets belonging to the rhombic system; even where the mass appears to be an amorphous powder, the microscope and also the peculiar soapy feeling between the fingers show it to consist of very fine crystalline scales. It is frequently accompanied by crystals of quartz, and if the original felspar rock or its admixed minerals contained iron, the kaolin is coloured more or less yellow, red, or green by the presence of ferric or ferrous oxides. Kaolin is found in China, near the Kauling Mountains, whence its name is derived; in Europe the finest china clay is found in Yrieux near Limoges, and it is from this that the celebrated Sèvres porcelain is made; good china clay is likewise found in Cornwall, Saxony, various localities in America, and elsewhere. The following table gives the composition of some varieties:

	SiO_2.	Al_2O_3.	H_2O.	$(K,Na)_2O$.	Fe_2O_3.	$(Ca,Mg)O$.
$H_2Al_2Si_2O_8 + H_2O$ . .	46·4	39·7	13·9	—	—	—
Kaolin from China .	50·6	32·7	10·0	2·5	2·6	0·8
,, ,, Yrieux .	48·4	34·9	12·6	2·4	1·3	—
,, ,, Cornwall .	46·4	38·6	9·1	1·8	—	3·5
Cornwall Clay . .	45·8	39·4	14·3	—	—	—
Dorsetshire blue clay .	46·4	38·0	13·4	—	1·0	1·2

Ordinary clay consists of a mixture of kaolin with silica, ferric oxide, calcium carbonate, magnesium carbonate, and organic matter. Thus Stourbridge clay used for making crucibles, fire-bricks, gas retorts, &c., contains approximately 40 per cent. of free silica and 60 per cent. of kaolin. Kaolin kneaded to a paste with water forms a plastic mass easily cut, pressed to any shape, squirted by pressure through dies to form rods or tubes, cut into lengths to make bricks, &c.; when gradually dried such worked clay does not crumble and when the articles are subsequently heated to drive off the combined water they shrink about 10 per cent. in their length and bake into a hard porous solid. At all ordinary furnace temperatures, kaolin cannot be fused, but the presence of very small quantities of foreign materials induces partial fusion so that the mixture becomes more or less soft and pasty in the furnace; oxide of iron particularly has this effect, as well as lime and the alkalis. Upon his skill in choosing and admixing certain fusible materials with kaolin and impure clays the success of the potter depends.[1]

[1] For a fuller account of Pottery and Porcelain, consult Burton's article in Vol. IV. of Thorpe's *Dictionary of Applied Chemistry* (1913).

338 *History of Earthenware, Pottery, and Porcelain.*—The potter's art is one of the oldest in existence. The Egyptians were well acquainted with the means of glazing ware made of burnt clay, as well as with the art of enamelling in colours. Amongst European nations the Etruscans were especially celebrated in early times for their proficiency in the manufacture of painted pottery ware, and in Pliny's time several towns in Greece and Italy were well known for the beauty and artistic taste of their vases, urns, and other pottery wares.

Porcelain was not known to the Romans, although the Chinese have manufactured it for ages, and the Egyptian tombs contain remains of vessels made of a material closely allied to porcelain. The art of glazing pottery with the oxides of lead and tin was generally practised in Europe during the Middle Ages, and we find a description of the process then adopted in the writings of the alchemists Peter Bonus and Albertus Magnus at the beginning of the thirteenth century. In the following century the potter's art made great strides. Agricola published many receipts concerning this manufacture; amongst others, he states not only that a mixture of litharge with tin oxide gives a good glaze, but that the former oxide may be employed alone for this purpose.

Amongst those who have been most active in promoting the progress of the ceramic art the name of Bernard Palissy stands pre-eminent. Devoting himself with self-sacrificing assiduity to the production of glazed and coloured faience, Palissy laid the foundation of modern art pottery. His numerous writings, published during the latter half of the sixteenth century, spread a knowledge of his experimental methods throughout Europe; but his works *L'Art de Terre et des Terres d'Argile* are confined to a description of the manufacture of earthenware; it was not until the year 1709 that the method of making porcelain was discovered by Böttticher, and in the following year the celebrated porcelain manufactory at Meissen, in Saxony, was established.

The mode of preparation of the Meissen porcelain being naturally kept secret, the King of Prussia instructed the celebrated chemist Pott to determine the nature of the materials used, and he, being unable to obtain any satisfactory information, was obliged to investigate the properties of those substances which might possibly be used in the manufacture, mixed in varied proportions; for this purpose Pott is said to have made no less than 30,000 experiments. To these we are mainly indebted

for the establishment of the reactions which occur when various minerals are heated, and much valuable information applicable to the manufacture of porcelain was thus obtained. About the same time Réaumur endeavoured to ascertain the secret of porcelain-making, and found that it is produced by the union of two earths, one of which is fusible, whilst the other is infusible at the same temperature, so that by the firing of an intimate mixture a non-porous, translucent mass is formed.

His investigations were taken up in the year 1758 by Lauraguais, D'Arcet, and Legay, in France, and by the help of Macquer they succeeded in re-discovering the art of porcelain-making, and in the year 1769 the celebrated porcelain manufactory of Sèvres was founded.

Even up to the beginning of the nineteenth century real porcelain was a material of great rarity and value. At the present day, however, it is cheap, and is employed for making the most ordinary articles of everyday use.

Hard Porcelain or *True Porcelain* is distinguished by its fine and hard translucent structure, and is with difficulty attacked by chemical reagents. According to Emmerling's experiments water and acids, even when boiled, have next to no action on porcelain, and it is attacked by alkalis less powerfully than glass, and hence in chemical and analytical operations the use of porcelain is much to be preferred to that of glass. Porcelain also stands rapid alteration of temperature without cracking, and this property is one of extreme value to chemists; whilst its beauty, and the fact that its surface is capable of taking colours which will stand firing, render it of great importance in the manufacture of objects of art.

In the manufacture of porcelain the infusible kaolin is mixed with a frit, flux, or fusible material, consisting of a silicate. This on fusion penetrates into the pores of the heated clay, producing a hard, apparently homogeneous, translucent mass lustrous on its fractured faces. The name porcelain is derived from a Portuguese word *porcellana*, a shell which is similar in general appearance to porcelain. The ordinary flux employed is felspar, but other materials may be admixed with it, depending upon the composition of the kaolin employed.

When a mixture has proved to be successful, each manufacturer adheres strictly to his special receipt, not only because an alteration in the proportions would render a different temperature necessary for burning, but especially because it would

also entail a variation in the shrinking of the mass, and as the manufacturer has frequently to prepare his wares to pattern, it is necessary to keep to one rate of shrinkage. On the determination of the purity of the materials and of the fire-resisting power of clays Bischof and Richters [1] have published elaborate investigations, to which we must refer the reader.

The greatest care has to be taken in the thorough mixing of the materials, and in obtaining them in a very finely-divided state. For this purpose they are ground together with water to a thin cream which is passed through very fine sieves, and the excess of water is then got rid of by means of a special pattern of filter press. The lumps of moist material are then stocked ready to be worked up on the potter's wheel, or brought into the requisite shape by pressing into moulds, and the objects thus prepared are allowed to dry at the ordinary temperature before being fired in the upper portion of the porcelain kiln. The fired goods are then dipped into water containing the finely-divided glaze in suspension. The composition of porcelain glaze is seen in the following table:

Sèvres.	Meissen.		Berlin.	
Pure ground felspar.	Quartz	37	Quartz	43
	Kaolin from Seilitz.	37	Kaolin from Morl . .	31
	Lime	17·5	Gypsum	14
	Broken porcelain .	8·5	Broken porcelain . .	12
		100·0		100

The articles are dried and exposed to a higher temperature in the porcelain kiln, which consists essentially of a high reverberatory furnace. The flame and hot gases surround the earthenware "seggars," or infusible crucibles, in which the porcelain ware is placed to protect it from the smoke and direct action of the flame. When the temperature has reached its maximum, the kiln with its contents is bricked up, and the whole allowed to cool very slowly. This annealing process is necessary, as the glaze forms a true glass, and if the heated mass were quickly cooled the porcelain would be brittle from the unequal tension of its different parts.

Painting on porcelain is a branch of the art of glass-staining and the same substances are employed for painting upon porcelain as are used in colouring glass. They are divided into two classes: (1) Those which are not destroyed at the temperature

[1] C. Bischof, *Dingl. Polyt. Journ.*, **159–211**; Richters, *ibid.*, **191–197**.

of the porcelain kiln, and can be painted on the ware below the glaze—these are termed refractory colours, and include cobalt-blue, chrome-green, the brown produced by oxide of iron or manganese, chromate of iron, &c., and uranium black; and (2) those colours which are injured when heated above a certain temperature—these are termed muffle-colours, because they are fixed on the glazed ware by a separate firing at a lower temperature in a muffle. The following substances are used as muffle-colours: iridium oxide, cupric oxide, cuprous oxide, chromate of lead, silver chloride, purple of Cassius, &c., and an admixed flux for these is employed, consisting of quartz or sand, borax or boric acid, felspar, litharge or red lead, nitre and the carbonates of potassium and sodium, in suitable proportions.

Tender or *Fritted Porcelain.*—This form of porcelain was first prepared in 1695, by Morin in St. Cloud. The mass resembles that of true china, but the frit and glaze are much more fusible. This is the kind of porcelain specially manufactured in England. The materials employed in this manufacture are: (1) The mass or body, composed of Cornish stone, China clay, or decomposed pegmatite. (2) The frit or fusible material, consisting of bone ash or mineral phosphate with, sometimes, the addition of borax. (3) The glaze, consisting of bone ash, sand, borax, potashes, and lead oxide. The following are mixtures in use for English china:

	I.	II.	III.
Bone ash . . .	47	41	47·3
Cornish stone .	31	30	—
China clay . .	22	29	33·8
Felspar	—	—	18·9
	100	100	100·0.

The glaze used for English table ware consists of:

Cornish stone	34
Chalk	17
Ground flint	15
Borax	34
	100.

These materials are fritted, ground, and mixed with 10 per cent. of Cornish stone and 20 per cent. of white lead.

Parian or *Carrara Biscuit-ware* is a white unglazed porcelain,

less fusible than ordinary tender porcelain and largely used for the preparation of statuettes.

Stoneware is distinguished from porcelain by its opacity, due to the fact that the mass is not nearly so finely ground and consequently not so intimately mixed with the frit as is the case with porcelain. The materials used are the plastic clays and pipe-clays found in large quantity in the coal-measures, and these are mixed with a frit which is either felspathic or may contain lead or borax, the proportion of frit used being larger than in the case of porcelain. The mass often contains quartz granules of considerable size, and the materials used are not specially selected to be particularly free from iron oxides. Stoneware is therefore much cheaper than porcelain and is largely used for the construction of chemical manufacturing plant, such as condensing tubes and bottles for hydrochloric and nitric acids, evaporating pans, centrifugal machines, large store tanks, cooling worms, pumps, injectors, fans, taps, &c.

Semi-porcelain.—This is a fine kind of stoneware, prepared from a white plastic clay, to which ground quartz or flint, or even felspathic stone, is added in the requisite quantity. After the first burning it is porous and adheres to the tongue. It is then glazed with a transparent glaze consisting of borax, quartz, soda, and oxide of lead.

Earthenware or *Common Pottery Ware.*—This material is like the foregoing, inasmuch as it is porous, but it is comparatively soft and easily broken or cut by steel tools and will not long withstand the action of strong chemicals. Earthenware is made from a coloured plastic clay the impurities of which act as the frit, and in order to diminish the shrinking it is frequently mixed with marl, *i.e.*, a clay containing a considerable proportion of admixed sand grains. It is glazed by throwing common salt into the kiln when the burning is nearly complete. This is volatilised and decomposed by the aqueous vapour and the products of combustion, with formation of hydrochloric acid and soda, which latter unites with the clay to form a sodium aluminium silicate. It may also be glazed with a lead glaze. Earthenware is largely used for agricultural drain-pipes, tiles, bricks, flower-pots, and in the glazed form for pans and basins for domestic use.[1]

[1] Consult the article "Fritts and Glazes," in Vol. II. of Thorpe's *Dictionary of Applied Chemistry* (1912).

Faience is an opaque, porous, generally soft body pottery, always coloured, with either a glaze rendered white and opaque by tin or sometimes by calcium phosphate (*faicnce émaillée*), or else a transparent lead glaze. In this latter case a slip of finer clay generally covers the coarse body. It was known and manufactured in the 9th century by the Arabians, and the knowledge of the manufacture passed with the Moors into Spain, and established itself in the Island of Majorca, whence the name *Majolica* is derived, being the old Tuscan name for this island. The same ware in Italy was named faience from the name of the town of Faenze, where the industry was established in the 13th century, and flourished until the 15th. In France, the manufacture was commenced by Bernard Palissy, in the 16th century.

Crucibles.—The various kinds of melting crucibles which are made of clay have a special interest to the chemist. These require to be made of material which will stand a very high temperature without softening or breaking up, and is capable of withstanding rapid changes of temperature. The well-known Hessian crucibles are made of a clay containing about 71 parts of silica, 25 of alumina, and 4 of oxide of iron, and this is mixed with one-third to one-half its weight of quartz sand, while plumbago crucibles are made of a finer and purer clay admixed with plumbago scales which serve to knit the clay together instead of a frit.

Ultramarine.

339 A double silicate of aluminium and sodium containing sulphur, known as *lapis lazuli*, has long been valued for its splended blue colour. Its constitution is, however, as yet unknown. It crystallises in dodecahedra, but usually occurs in the massive condition, and is found in Central Asia, Siberia, Persia, China, &c. It is largely used for making vases and for inlaying ornamental furniture, and the powdered lapis lazuli forms a valuable paint termed ultramarine. This substance is, however, now artificially prepared on a large scale.

Tassaert observed in 1814 the formation of a blue colour in one of his black-ash furnaces at the celebrated glass-works of Saint Gobain, and Vauquelin showed that this colour was identical with lapis lazuli. In 1824 a prize was offered in France for the discovery of a practical method of manufacturing this colour, and this problem was successfully solved in the year 1828

simultaneously by Guimet[1] and Christian Gmelin, the latter of whom published the process in the year 1828.[2]

Since this date the ultramarine industry has largely increased. The chief quantity of the substance is manufactured in Germany, and the total production now amounts to about 10,000 tons per annum. In the year 1829 the price of artificial ultramarine was £12 per lb., whereas now it is sold at less than 30*s.* per cwt. Different varieties of ultramarine occur in commerce; these, however, can be divided into two classes.

Ultramarine poor in silica is obtained by heating a mixture of soft clay with Glauber's salt, charcoal, soda, and sulphur in crucibles placed in a furnace. Instead of charcoal, tar or resin is sometimes employed. In this way a colourless compound is first produced, termed white ultramarine. This, however, soon becomes of a green colour. The green ultramarine thus obtained, which is also used as a colour, is then mixed with sulphur and heated. The sulphur takes fire and is allowed to burn in the air, when the product becomes of a fine blue colour. *Ultramarine rich in silica* is generally obtained by heating a pure clay with finely ground white sand, sulphur, and resin or charcoal in a muffle furnace, when a blue product is at once obtained which, according to the quantity of silica originally added, retains more or less of a red tinge. The different kinds of both green and blue ultramarine are then finely ground and washed with water, and thus the several marketable varieties are obtained. A violet and a red variety of ultramarine have also been prepared. The following table gives the composition of some different ultramarines:

		Blue.	
	Green.	Poor in Silica.	Rich in Silica.
SiO_2	38·52	37·90	40·77
Al_2O_3	28·94	29·30	23·74
Na_2O	23·68	22·60	18·54
S	8·30	7·86	13·58
Earthy residue	1·94	2·36	3·61
	101·38	100·02	100·24.

The ultramarine which is poor in silica is decolorised by the action of a cold solution of alum, whilst the ultramarines rich

[1] *Ann. Chim. Phys.*, 1831, **46**, 431.
[2] *Quart. Journ. Science*, 1828, **2**, 216.

in silica withstand the action of this salt, and the more completely the more silica they contain. Hence these latter varieties are employed in cases in which the colouring matter comes in contact with aluminium salts, as, for instance, the blueing of paper and in calico-printing. The different kinds of ultramarine are very largely employed in the arts for water-colours, as oil-paint, and for paper-staining.

It has already been stated that the chemical constitution of ultramarine is, as yet, unknown.[1] The sulphur present is, however, contained in two conditions. Dilute acids readily decompose all the different kinds of ultramarine, gelatinous silica and finely-divided sulphur being deposited and sulphuretted hydrogen evolved, but on the other hand concentrated sulphuric acid and glacial acetic acid have no action upon ultramarine.[2]

Silver-Ultramarine.—When blue ultramarine is heated with a solution of silver nitrate, the sodium is replaced by silver, and a yellow powder is thus obtained which under the microscope is seen in the form of dark lemon-yellow transparent particles.[3] It is easily decomposed by acids with separation of silica, one-third of the silver being precipitated as silver sulphide, but without evolution of sulphuretted hydrogen. If silver ultramarine be heated with a solution of potassium chloride the silver is replaced by potassium, and in this way blue potassium ultramarine is obtained, a substance which has hitherto not been prepared directly (Heumann). A bright blue lithium ultramarine has also been prepared in similar manner. Organic derivatives of ultramarine, such as ethyl ultramarine, have also been obtained from the silver compound by the action of the alkyl iodides. Ultramarines containing selenium and tellurium in place of sulphur have been prepared.

The preparation of these substituted ultramarines has not, however, led to the recognition of the chemical nature of ultramarine. The difficult problem as to the constitution of this remarkable coloured compound has indeed not yet been solved. It has been suggested that the colouring matter of both natural and artificial ultramarine is a double compound of a sodium aluminium silicate and sodium sulphide, which has been variously formulated as $2Na_2Al_2Si_2O_8,Na_2S_2$ (Heumann)

[1] See article "Ultramarine," *Thorpe's Dict. of Applied Chem.*, and Abegg, *Handbuch* (1906), **3**, 120, where references are given to the literature of the subject.

[2] Hofmann and Metzener, *Ber.*, 1905, **38**, 2482.

[3] See Chabrié and Levallois, *Compt. rend.*, 1906, **143**, 222.

and $Na_4(NaS_3Al)Al_2(SiO_4)_3$ (Brögger and Backström),[1] the latter formula being closely analogous to that of haüyne, $Na_2Ca(NaSO_4Al)Al_2(SiO_4)_3$, a mineral which is also characterised by a blue colour. The existence of a definite compound of this formula in ultramarine has, however, not been proved, and it has been suggested that the blue colour is due to some comparatively simple substance, possibly elementary sulphur, disseminated throughout a colourless medium.[2]

Hoffmann[3] considers that the colour is due to colloidal sulphur.

Detection and Estimation of Aluminium.

340 Aluminium compounds do not impart any colour to the non-luminous gas-flame. The spark spectrum of aluminium has been mapped by Thalén, Kirchhoff, and Lecoq de Boisbaudran, and its spectrum in the electric arc by Liveing and Dewar and by Kayser and Runge. The last-named investigators found that the visible portion of the spectrum did not contain a single line. The aluminium bands in the ultra-violet, however, are extremely characteristic. These are contained in the invisible and highly refrangible portions of the spectrum which are only seen when the rays are allowed to fall on a fluorescent substance.[4] Alumina also shows a characteristic spectrum even in the arc.

Aluminium occurs almost always combined with oxygen. Most of these compounds are insoluble in water; many of them, however, are decomposed by hydrochloric acid, the alumina entering into solution. Those compounds which withstand the action of acids are decomposed by fusion with sodium carbonate and treatment of the fused mass with hydrochloric acid. Corundum, spinel, and some other minerals are not, however, decomposed in this way, but must be fused with hydrogen potassium sulphate.

Aluminium can readily be separated from all other metals. It is not precipitated from its acid solutions by sulphuretted hydrogen, whereas it is completely thrown down as the hydroxide by ammonia and ammonium sulphide, and thus can be readily separated from the metals of the alkalis and alkaline earths. It is

[1] *Zeit. Kryst. Min.*, 1891, **18**, 209. [2] Abegg, *Handbuch* (1906), **3**, 128.
[3] *Zeit. Chem. Ind. Kolloide*, 1912, **10**, 275.
[4] Stokes, "On the Long Spectrum of the Electric Arc," *Phil. Trans.*, 1862, **152**, 599.

distinguished from most of the metals precipitable by ammonium sulphide, inasmuch as its hydroxide is soluble in caustic alkalis. This property it possesses in common with the hydroxides of zinc, chromium, and glucinum. The first of these metals is precipitated from the alkaline solution by sulphuretted hydrogen, and chromium hydroxide is only soluble in the cold, and is precipitated on boiling. If to the solution from which the zinc and chromium have thus been separated, hydrochloric acid and then ammonia be added, the aluminium is precipitated. This precipitate may, however, still contain glucinum hydroxide, which must be dissolved by digesting it with ammonium carbonate or sodium bicarbonate (p. 620). When the oxide is strongly heated with a salt of cobalt a bright blue mass is obtained.

For quantitative estimation, aluminium is precipitated as hydroxide, and then converted into the oxide by strong ignition.

The Atomic Weight of aluminium was first determined by Berzelius in 1812, who found that 100 parts of the anhydrous sulphate yielded 29·934 parts of pure alumina, according to which the atomic weight is 27·1.[1] Tissier [2] found the number 27 by the conversion of the metal into the nitrate and then into the oxide, and Dumas [3] 27·3 by the analysis of the chloride. The most reliable determinations are due to Mallet,[4] who employed three distinct methods : the ignition of ammonium alum, which gave the number 26·89 ; the analysis of the bromide, from which the atomic weight appeared to be 26·91 ; and finally, the direct determination of the equivalent to hydrogen. This last set of experiments was carried out by dissolving pure aluminium in concentrated aqueous soda and collecting and measuring the dry hydrogen produced. He thus found that 3·352 grm. of aluminium yielded 4161·6 c.c. at the normal temperature and pressure (in 45° north latitude). According to this, the equivalent of aluminium is 8·969 and the atomic weight 26·91. In a second series of less reliable experiments the hydrogen was burned and the water weighed. Finally Thomsen [5] determined the ratio Al : H and Al : O independently by dissolving metallic aluminium in concentrated caustic potash solution and finding the weight of hydrogen evolved and the weight of oxygen required to burn the hydrogen. He used a somewhat impure

[1] *Pogg. Ann.*, 1812, **8**, 187.
[2] *Compt. rend.*, 1858, **46**, 1105.
[3] *Ann. Chim. Phys.*, 1859, [3], **55**, 151.
[4] *Phil. Trans.*, 1880, **171**, 1003.
[5] *Zeit. anorg. Chem.*, 1896, **11**, 14 ; 1897, **15**, 447.

aluminium and after allowing for the effect of the impurity, obtained somewhat lower numbers than Mallet—

$$Al : H = 26{\cdot}770 : 1\,;\quad Al : O = 26{\cdot}992 : 16.$$

The most probable value is at present (1913) taken as 27·1.

GALLIUM. Ga = 69·9.

341 This metal, the eka-aluminium of Mendeléeff (p. 68) was discovered in 1875 by Lecoq de Boisbaudran by means of spectrum analysis. He found the new element in the zinc blende of Pierrefitte in the Pyrenees and patriotically gave to it the name which it now bears. It is found also in the blende from other localities. Thus a yellow transparent blende from the Asturias and a black blende from Bensberg contain it, and that from Bensberg, although the richest, contains only 16 mgr. of gallium per kilo.; it occurs also in a grey zinc ore found at Pulwood, New South Wales.[1]

An examination of the spectrum yielded by a large number of minerals in the oxyhydrogen flame has revealed the fact that gallium, like lithium and rubidium, is very widely distributed in nature, although present only in very minute quantities. It occurs, for example, in a large number of iron ores, from which it passes into the iron prepared from them, so that Middlesbrough cast iron contains as much as 1 part of gallium in 33,000 parts and is the richest source of this element known.[2] It also occurs constantly in bauxite and the aluminium salts prepared from it, as well as in kaolin, and in zinc blende, and is occasionally found in pyrites and manganese ores. It is present also in all meteoric irons, but not in all meteorites.[3]

In order to prepare gallium, the ore, according to its physical character, is dissolved either in aqua regia, hydrochloric acid, or sulphuric acid, and the solution decomposed by means of metallic zinc. The precipitate thus thrown down, which contains most of the foreign metals present in the blende, is then treated with hydrochloric acid, and the liquid again precipitated with zinc in the cold. As soon as the evolution of hydrogen becomes feeble the solution is poured off from the precipitate and

[1] Kirkland, *Austr. Assoc. Adv. Sci.*, 1893, 266.

[2] Hartley and Ramage, *Proc. Roy. Soc.*, 1897, **60**, 35, 393; *Journ. Chem. Soc.*, 1897, **71**, 533, 547.

[3] *Sci. Proc. Roy. Dublin Soc.*, 1898, N.S., **8**, 703.

saturated with sulphuretted hydrogen, the precipitate filtered off, the excess of sulphuretted hydrogen expelled, and the liquid fractionally precipitated with sodium carbonate in the cold until the precipitate thrown down no longer exhibits the gallium line when examined with the spectroscope. It is then dissolved in sulphuric acid, gently heated until the excess of sulphuric acid is almost completely removed, the residue treated for some time with cold water, and the solution diluted with water, and then heated to boiling, when basic gallium sulphate separates out, which must be filtered off whilst hot. This precipitate is dissolved in a small quantity of sulphuric acid; to this liquid a slightly acid solution of ammonium acetate is added, sulphuretted hydrogen passed through to saturation, the solution filtered, and the filtrate, diluted with water, heated to boiling, the precipitate which forms being washed with boiling water. This is then dissolved in a small quantity of sulphuric acid, a slight excess of alkali added, and the alkaline solution submitted to electrolysis. Metallic gallium is thus deposited at the negative pole, and in order to obtain it in the perfectly pure state it is treated with warm dilute nitric acid free from chlorine. Sixty-two grms. of gallium were exhibited in the Paris Exhibition of 1878, having been prepared from 2,400 kilos. of blende by Lecoq de Boisbaudran and Jungfleisch.[1]

Metallic gallium possesses a bluish-white colour, and has the remarkable property of fusing at 30·1°. The molten metal possesses the colour of silver and remains liquid for many weeks at the ordinary temperature, and even when exposed to 0°. If, however, the globule be touched with a small fragment of solid gallium it at once solidifies, forming pyramidal crystals, probably belonging to the monoclinic system.

Gallium is tough and may be cut with a knife ; the molten metal, when brought on to glass, covers the surface with a bright mirror-like deposit, and oxidises on exposure to the air. It is not volatile at a red-heat, and only a thin film of oxide is formed on the surface. Its specific gravity is 5·9, and its specific heat 0·080. It is easily soluble in dilute hydrochloric acid and caustic potash with evolution of hydrogen. It is scarcely attacked by dilute nitric acid in the cold, but on heating it slowly dissolves with evolution of red vapours. If a neutral solution of gallium chloride is warmed with zinc, gallium oxide, or a basic salt separates out, but not the metal.

[1] *Compt. rend.*, 1878, **86**, 475.

GALLIUM COMPOUNDS.

342 *Gallium Oxide*, Ga_2O_3, is a white mass, which is reduced to the metal by hydrogen at a bright red heat. The hydroxide is a white precipitate insoluble in water, but readily soluble in potash, and somewhat less so in ammonia.

Gallium Trichloride, $GaCl_3$.—Like aluminium, but unlike indium, gallium yields the trichloride when heated in hydrogen chloride as well as in chlorine, long needle-shaped crystals being deposited in the tube close to the flame. It is a very deliquescent substance and dissolves in a small quantity of water to form a clear liquid, which on the further addition of water becomes turbid from deposition of a basic salt. It melts at 75·5°, and boils at 215–220°. The vapour density of gallium chloride, as determined by the air-displacement method, is 6·1 between 440–606°, and corresponds to the formula $GaCl_3$. Like aluminium chloride its density near the boiling point is somewhat higher than this, being 8·8 at 350°.[1]

Gallium Dichloride, $GaCl_2$, is obtained by the action of the metal on the trichloride and melts at 164°, forming a limpid refractive liquid which boils at 535°. The specific gravity of its vapour is 4·8 at 1,000°, corresponding to the formula $GaCl_2$.

Gallium Sulphate is also very soluble but non-deliquescent. It combines with ammonium sulphate to form an alum, $Ga_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, which crystallises in combinations of the cube and octahedron. If its solution is boiled a precipitate is produced consisting probably of basic sulphate.

Gallium Nitrate is also a soluble well-crystallised salt.

The best means of detecting gallium is the spark spectrum of the chloride or other salt. This consists of two violet lines (4171, 4031), of which the brightest, Gaα, lies a little more towards the blue than the line Inβ, and the second Gaβ rather more towards the violet than Kβ. In the non-luminous gas-flame the chloride gives only a very slight indication of the line Gaα.

The Atomic Weight of gallium has been determined by Lecoq de Boisbaudran[2] by igniting the ammonium alum, and also by dissolving the metal in nitric acid and igniting the residue, the oxide obtained in both cases being weighed. The first determination gave the atomic weight 69·6, and the second 69·2. The number at present (1913) adopted is 69·9.

[1] Nilson and Pettersson, *Journ. Chem. Soc.*, 1888, **53**, 824.

[2] *Bull. Soc. chim.*, 1878, **29**, 9.

INDIUM. In = 114·8.

343 This metal was discovered in Freiberg zinc blende in the summer of the year 1863 by Reich and Richter by means of spectrum analysis.[1] Indium also occurs as sulphide in other zinc blendes, although present only in very small quantity. It has also been detected spectroscopically in a manganese ore of Spanish origin and in a number of samples of siderite, which were obtained from various localities and all contained manganese.[2] In order to prepare indium it is best to employ metallic zinc, such as that from Freiberg, which, however, does not contain more than 0·1 per cent. The metal is treated with such a quantity of hydrochloric acid that a small portion remains undissolved, and when the solution is allowed to stand for two or three days the whole of the indium is found to be precipitated on the residual zinc. The metallic powder is then washed off from the zinc, and a few drops of dilute sulphuric acid are added to dissolve any basic zinc chloride which may be formed; the spongy metal is well washed with hot water, then treated with nitric acid, and the acid solution, without filtration, is boiled down with an excess of sulphuric acid until all the nitric acid is driven off. The solution is then filtered, the residue well washed, and a large excess of ammonia added to the filtrate. The zinc, cadmium, and copper remain in solution whilst the whole of the indium, together with iron, lead, and a small quantity of zinc, cadmium, and copper, remains behind. After being well washed, the residue is dissolved in a small quantity of hydrochloric acid, an excess of hydrogen sodium sulphite added, and the solution boiled until it no longer smells of sulphur dioxide. A precipitate is thus obtained of basic indium sulphite, which for further purification may be dissolved in sulphurous acid; on boiling this solution the pure salt separates out,[3] and this when strongly heated decomposes, leaving a residue of indium trioxide. The oxide can then be reduced to metal by ignition in a current of hydrogen or by fusion with sodium. The latter method appears to be the best suited for the preparation of large quantities. For this purpose the finely-divided oxide is placed in layers in a crucible with thin slices of sodium, the mixture pressed down and then covered with a thick

[1] *J. pr. Chem.*, 1863, **89**, 444; **90**, 172; 1864, **92**, 480.
[2] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533.
[3] Bayer, *Annalen*, 1871, **158**, 372.

layer of anhydrous sodium chloride. The porcelain crucible is next placed in a Hessian crucible provided with a cover, and heated first gently and, as soon as the reaction is over, to a moderate red-heat. The brittle alloy which is then obtained is boiled several times with water, washed with alcohol and ether, and again fused under a layer of potassium cyanide. The regulus is still not quite free from sodium, and in order to remove these traces it is thrown, in small pieces, into fused sodium carbonate, and the metal thus obtained in the pure state.[1]

The pure metal may also be separated electrolytically from solutions of the chloride or nitrate containing pyridine, hydroxylamine, or formic acid,[2] or from a solution of the sulphate.[3]

Indium is a white metal, easily malleable and softer than lead. It is obtained crystallised in regular octahedra [4] by the electrolysis of the sulphate, a branched metallic "tree" being formed. Its specific gravity at 13°/4° is 7·12, and its melting point 155°. It retains its metallic lustre in the air and even in boiling water. Heated on charcoal before the blowpipe it colours the flame blue and gives an incrustation of the oxide. It dissolves slowly in hydrochloric and dilute sulphuric acids, but readily in nitric acid.

INDIUM COMPOUNDS.

344 *Indium Oxide*, In_2O_3, is a pale yellow powder, which on heating becomes brown, but regains its original colour on cooling. After ignition it dissolves only slowly in cold dilute acids, but quickly when the acid is warmed. According to Renz,[5] two other modifications of the amorphous oxide are formed when the yellow oxide is very strongly heated, both of these being white powders, one soluble and the other insoluble in dilute acids. The oxide begins to volatilise perceptibly at about 1000° and becomes partially crystalline (Thiel). It appears to melt at a higher temperature than alumina.

[1] Winkler, *J. pr. Chem.*, 1867, **102**, 273

[2] Dennis and Geer, *Ber.*, 1904, **37**, 961.

[3] Thiel, *Zeit. anorg. Chem.*, 1904, **40**, 280.

[4] Sachs, *Zeit. Kryst. Min.*, 1903, **38**, 495.

[5] *Ber.*, 1903, **36**, 1847. Compare Thiel, *Zeit. anorg. Chem.*, 1904, **40**, 324; Meyer, *ibid.*, 1905, **47**, 281.

Indium Hydroxide, $In(OH)_3$, is formed when ammonia or dimethylamine is added to a soluble indium salt. The hydroxide is thrown down as a gelatinous precipitate, which on boiling becomes heavy and dense, and when heated is easily converted into the oxide. It dissolves in caustic potash,[1] but not in ammonia, and readily forms colloidal solutions in the absence of electrolytes. When the oxide is heated in a current of hydrogen at 300° a black pyrophoric powder is obtained, which appears to contain the lower oxide, InO.

Indium Trichloride, $InCl_3$.—The metal burns at a dull red heat in a current of chlorine, evolving a greenish-yellow light with formation of the chloride. The same compound is easily formed by heating the oxide, mixed with charcoal, in chlorine. It sublimes at about 446° in the form of soft colourless plates, is extremely deliquescent, and dissolves in water with a hissing noise and evolution of heat. On evaporating the solution an insoluble basic salt is obtained. The vapour density of indium trichloride was found by V. and C. Meyer[2] at a bright red heat to be 7·87, corresponding to the formula $InCl_3$. An *oxychloride*, InOCl, is formed as a white powder by the action of chlorine and oxygen on the dichloride (Thiel).

Indium Dichloride, $InCl_2$, is obtained as a white radiating crystalline mass by heating the metal in a current of hydrogen chloride. The vapour density of the dichloride has been shown by Nilson and Pettersson[3] to be 6·43 at 1300°, corresponding to the above formula. This compound is decomposed by water with formation of the trichloride and separation of metallic indium:

$$3InCl_2 = 2InCl_3 + In.$$

Indium Monochloride, InCl, was prepared by the above-named chemists by distilling the vapour of the dichloride over the requisite amount of metallic indium; combination takes place, and the monochloride is obtained in the form of a mass resembling hæmatite, which melts to form a blood-red liquid and can readily be vaporised. Its vapour density was found to be 5·5–5·3 at 1100–1400°. The monochloride undergoes a similar decomposition to the dichloride when brought into contact with water, the trichloride and metallic indium being formed:

$$3InCl = InCl_3 + 2In.$$

[1] See Renz, *Ber.*, 1901, **34**, 2763. [2] *Ber.*, 1879, **12**, 611.
[3] *Journ. Chem. Soc.*, 1888, **53**, 814.

Indium combines also with bromine and iodine when heated in the vapours of these elements. The three *bromides* closely resemble the chlorides, and the *tri-iodide* is a yellow crystalline mass, which on heating melts to form a reddish-brown liquid. A sparingly soluble *fluoride*, InF_3, crystallising with $9H_2O$ or $3H_2O$, is formed when the oxide is dissolved in hydrofluoric acid.[1]

Indium Nitrate, $2In(NO_3)_3,9H_2O$, forms deliquescent needles soluble in both water and absolute alcohol. These on heating are easily converted into a basic salt.

Indium Sulphide, In_2S_3.—Pure indium and sulphur combine together at a temperature near redness, with evolution of heat, to form a bright-red infusible mass, which is also produced when the oxide is heated in a current of sulphuretted hydrogen. This gas, passed into a solution of an indium salt which is not too acid or too concentrated, precipitates yellow indium sulphide, which on heating with ammonium sulphide is converted into the white hydrosulphide and is soluble in concentrated acids. A lower sulphide, In_2S, has been obtained mixed with a little of the normal sulphide, by heating the latter in hydrogen. It is a black, fusible mass, which is readily soluble in warm dilute acids (Thiel).

Basic Indium Sulphite, $In_2(SO_3)_3,In_2O_3,8H_2O$, is a crystalline powder, the preparation of which has been already described. It dissolves easily in aqueous sulphurous acid and separates out on evaporation in distinct crystals.

Indium Sulphate, $In_2(SO_4)_3$, is obtained by the careful evaporation of a solution of the trioxide in an excess of sulphuric acid, in the form of a white powder very soluble in water. On strongly heating it is converted into an insoluble basic salt. On evaporating the acid solution over sulphuric acid, deliquescent crystals of the acid salt having the composition $H_2In_2(SO_4)_4,8H_2O$ are deposited.

Indium Ammonium Alum, $In_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, is deposited in well-defined regular octahedra, which dissolve at 16° in half their weight, and at 30° in about a quarter of their weight of water, and melt at 36°.[2] If a solution is allowed to crystallise at this temperature crystals of the hydrate, $In_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$, separate out.

The sulphates of potassium and sodium form analogous salts

[1] Thiel, *Zeit. anorg. Chem.*, 1904, **40**, 331; Chabrié and Bouchonnet, *Compt. rend.*, 1905, **140**, 90.

[2] Rössler, *J. pr. Chem.*, 1873, [2], **7**, 14.

containing 8 molecules of water, but do not yield true alums, whilst cæsium and rubidium yield alums of the normal composition.[1]

Detection and Estimation of Indium.

345 The indium compounds are distinguished inasmuch as when moistened with hydrochloric acid they tinge the non-luminous gas-flame a dark blue colour. The spectrum consists of an intense indigo-blue line, Inα 4511, and a less intense violet line, Inβ 4102. It is from this property that the metal derives its name.

When heated on charcoal with sodium carbonate indium compounds yield white beads of the metal and a yellow incrustation of oxide. Very small quantities (0·00024 mgrm.) of indium can be detected microchemically by the formation of a double chloride of indium and rubidium which crystallises in colourless rhombic octahedra.[2] Zinc precipitates metallic indium from solutions of its salts. Caustic soda and potash precipitate the hydroxide, which partly dissolves in an excess, but is completely deposited again on boiling; it is insoluble in ammonia. This reaction is employed for the separation of indium from the other metals, as are also the formation of the insoluble basic sulphite (p. 754), the precipitation of a sulphide of indium which is insoluble in dilute acids, and the production of a precipitate with pyridine.[3]

The Atomic Weight of indium has been determined by Reich and Richter, as well as by Winkler[4] and Bunsen,[5] by converting the metal into the oxide. By dissolving in nitric acid and heating the nitrate Winkler obtained the number 113·6, whilst Bunsen obtained the number 113·8 (O = 16). The experiments of Thiel,[6] who used comparatively large amounts of carefully purified material, have shown that all these numbers are considerably too low, and that conversion of the metal into oxide is attended by considerable difficulties. The analysis of the chloride gave the number 115·05, whilst that of the bromide gave 114·81. The analysis by Mathers[7] of these same salts

[1] Chabrié and Rengade, *Compt. rend.*, 1900, **131**, 1300; 1901, **132**, 472.

[2] Kley, *Chem. Zeit.*, 1901, **25**, 563; see also Huysse, *Zeit. anal. Chem.*, 1900, **39**, 9.

[3] Dennis and Geer, *Ber.*, 1904, **37**, 961.

[4] *Jahresb.*, 1867, 260.

[5] *Pogg. Ann.*, 1870, **141**, 1.

[6] *Zeit. anorg. Chem.*, 1904, **40**, 280.

[7] *Ber.*, 1907, **40**, 1220.

prepared from indium purified by fractional electrolysis, gave the numbers 114·88 and 114·86, whilst lower and less reliable numbers were obtained by the conversion of the metal into the sulphate, and the analysis of the dichloride. At present (1913) the adopted number is 114·8.

THALLIUM. Tl=204·0.

346 Thallium was discovered in the year 1861 by Crookes[1] in a seleniferous deposit obtained from a sulphuric acid manufactory at Tilkerode in the Harz. Selenium was being prepared from this deposit, and a considerable residue was left when the material was distilled. This was supposed at first to contain tellurium, but examination with the spectroscope showed that a new element was present whose spectrum consisted of one bright green line, whence the name of the element, from θάλλος, a green twig. In 1862 Lamy,[2] who discovered the element independently of Crookes, published the results of his investigations. It was first believed that this element was a non-metal belonging to the sulphur group, but it was afterwards found to be a metal and was obtained in the metallic condition.

Thallium occurs in small quantities in many varieties of iron and copper pyrites, and in a few micas containing lithium. The mineral crookesite, discovered by Nordenskjöld[3] in a copper mine at Skrikerum, in Sweden, contains:

Tl	Se	Cu	Ag	
17·25	33·28	45·76	3·71	= 100·00.

Thallium is also found in the mineral lorandite, $TlAsS_2$, which accompanies realgar in Macedonia,[4] and occurs in traces in some iron ores, manganese ores, and zinc blendes.[5]

The mineral water of Nauheim, near Frankfort, as well as that of many other mineral springs, contains small quantities of thallium.

For the purpose of preparing thallium it is best to employ the

[1] "On the Existence of a new Element, probably of the Sulphur Group," *Chem. News*, 1861, **3**, 193.

[2] *Société Impériale des Sciences de Lille*, May 2 and 16, 1862.

[3] *Annalen*, 1868, **145**, 127.

[4] *Journ. Chem. Soc.*, 1896, **70**, ii., 30.

[5] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533.

flue dust from sulphuric acid works, in which pyrites containing thallium is burnt. The dust which contains selenium, arsenious oxide, and small quantities of many other metals in the form of oxides or sulphates, is repeatedly boiled out with water acidulated with sulphuric acid, the solution concentrated and the thallium precipitated with zinc, when it is deposited in the form of needles or glittering plates. Thallium may be obtained in a purer condition by boiling up the flue dust with water, and adding hydrochloric acid or common salt to the concentrated clear solution. The precipitate is washed and gradually dissolved in half its weight of hot sulphuric acid, and then heated until all the hydrochloric acid and the greater part of the free sulphuric acid has been driven off. The residue is next dissolved in water, the solution treated with sulphuretted hydrogen for the purpose of precipitating mercury, silver, arsenic, antimony, and bismuth, and ammonia then added to the filtrate to throw down any iron or alumina which may still be present. The filtrate, when concentrated, yields crystals of pure thallium sulphate, from which the metal may be obtained by deposition on zinc or by electrolysis.[1] According to Bunsen,[2] the solution of zinc sulphate obtained at the Juliushütte, at Goslar, contains 0·05 per cent. of thallium chloride, and if metallic zinc is allowed to remain in contact with the solution, copper, thallium, and cadmium are thrown down in the metallic state. The precipitated metals are then carefully washed with water and digested with dilute sulphuric acid to dissolve the last two metals. If potassium iodide is then added to this solution, thallium iodide separates out, and this on treatment with potassium cyanide yields pure metallic thallium.

It is stated that thallium occurs in almost all specimens of commercial platinum, sometimes to the extent of 0·1 per cent.[3]

Pure thallium has a bluish-white tint and a lead-like metallic lustre. It has the sp. gr. 11·8, and is crystalline, and so soft that it may be marked with the nail and leaves a streak on paper. It is malleable, but possesses little tenacity, and can only with difficulty be filed or sawn, as the particles stop up the interstices of the tool. It appears to exist in two modifications, the transition temperature being 226°; it melts at 303°,[4]

[1] See also Förster, *Zeit. anorg. Chem.*, 1897, **15**, 71.
[2] *Phil. Mag.*, 1865, [4], **29**, 168.
[3] Warren, *Chem. News*, 1887, **55**, 241.
[4] Petrenko, *Zeit. anorg. Chem.*, 1906, **50**, 133.

volatilises at a very high temperature, and may be distilled in a current of hydrogen. Its vapour density[1] at 1728° is 14·25, corresponding with the molecular formula Tl_2. The density has not yet been determined at a series of different temperatures, so that this molecular formula can only be considered as a superior limit. When heated before the blowpipe it oxidises, a pale reddish vapour being evolved which possesses a peculiar smell. It decomposes water at a red heat and dissolves readily in nitric and sulphuric acids, both dilute and concentrated, whilst it is less readily soluble in hydrochloric acid. It is slowly acted upon by alcohol in presence of air forming an alcoholate, which is liquid at ordinary temperatures. Thallium readily forms alloys with other metals, and amalgamates with mercury. The metal is usually kept under glycerine or petroleum oil, owing to its oxidisability.

THALLIUM COMPOUNDS.

347 Thallium forms two distinct series of compounds, one of the type RX_3, corresponding with the position of the metal as a member of the aluminium group, the other of the type RX, closely analogous in many respects to the corresponding compounds of the alkali metals, but frequently bearing a strong physical resemblance to the corresponding compounds of lead.

Thallous Compounds.

348 Many of these compounds resemble the compounds of lead in their physical properties. Thus the halogen compounds (with the exception of the fluoride) are very sparingly soluble in water, and the sulphide is an insoluble black powder. On the other hand, the hydroxide, the sulphate, and the carbonate are all soluble in water, and closely resemble the corresponding potassium salts; the sulphate, perchlorate, and phosphate are moreover isomorphous with the corresponding salts of that metal.

Thallium Monoxide, Tl_2O.—When the metal is exposed to the air its surface assumes a dull grey colour, due to the formation of this compound. It may be obtained in the pure

[1] Meyer and Biltz, *Ber.*, 1889, **22**, 725; Biltz, *Math. natw. Mitt. Berlin*, 1895, 37.

state by heating the hydroxide in absence of air to a temperature of 100°. It is a black powder melting at about 300°, and dissolves easily in water with the formation of the hydroxide. Bromine converts it quantitatively into thallic oxide.

Thallous Hydroxide, TlOH, is formed by the action of water upon the metal in presence of air. In order to prepare it in larger quantity a solution of the sulphate is precipitated with the necessary quantity of baryta water. It crystallises in long yellow needles having the formula $TlOH,H_2O$. It is readily soluble in water, and the solution is colourless and possesses a strong alkaline reaction, turning yellow turmeric paper brown. This brown colour disappears, however, after some time as the hydroxide destroys the colouring matter. Hence if turmeric paper is written upon with metallic thallium the writing at first appears brown but gradually disappears [1] (Erdmann).

Rabe [2] has prepared an oxide having the formula Tl_2O, by acting on a solution of thallous sulphate with H_2O_2 and potassium hydroxide. It has a bluish-black colour.

Thallous Fluoride, TlF, is formed by dissolving the carbonate in hydrofluoric acid. It crystallises in glittering octahedra and cube-octahedra. It dissolves in 1·25 parts of water at 15°, and less readily in boiling water. It melts on heating, and may readily be sublimed in a current of hydrogen fluoride.

Thallium Hydrogen Fluoride, $TlHF_2$, is formed by allowing a solution of the fluoride in aqueous hydrofluoric acid to evaporate in a vacuum over sulphuric acid. It crystallises in similar forms to thallous fluoride, and dissolves in its own weight of water.

Thallium Monochloride or *Thallous Chloride*, TlCl, is formed when the metal burns in chlorine, and separates out when hydrochloric acid is added to a tolerably concentrated solution of a soluble thallium salt, forming a white curdy precipitate which assumes a violet tint on exposure to light (Hebberling). It crystallises from hot saturated solutions in the form of cubes, and melts easily, yielding a yellowish liquid which on cooling solidifies to a white, shining, crystalline, somewhat flexible mass, having a specific gravity of 7·02 (Lamy) and boiling at 719–731°. Its vapour density has been found to be 8·5,[3] corresponding to the normal molecular weight. According to Hebber-

[1] *J. pr. Chem.*, 1863, **89**, 381.
[2] *Zeit. anorg. Chem.*, 1908, **58**, 23.
[3] Roscoe, *Proc. Roy. Soc.*, 1878, **27**, 426.

ling 100 parts of water dissolve the following quantities of the salt:

At	0°	16°	100°
TlCl	0·198	0·265	1·427.

It is less soluble in dilute hydrochloric acid, and hence the salt is precipitated from aqueous solution on addition of this acid. It is scarcely soluble in ammonia, and is insoluble in alcohol. It is readily converted by chlorine into thallic chloride, $TlCl_3$.

Thallous Bromide, TlBr, is a very pale yellow precipitate less soluble than the chloride, to which it possesses strong analogies. Dry bromine does not attack the metal so readily as chlorine, but in presence of water the metal is readily dissolved.

Thallous Iodide, TlI, is formed when thallium and iodine are heated together. It may also be obtained by precipitating a solution of a thallium salt with potassium iodide, when it is thrown down as a beautiful yellow crystalline powder, which passes at 168° into a red modification, the reverse change occurring on cooling. Both forms can exist in the metastable condition through a large range of temperature.[1] The red form melts at 190°. When precipitated from a hot solution containing potassium acetate it is deposited in the form of microscopic orange-yellow cubes or cube-octahedra (Werther). It is very sparingly soluble in cold water, 1 part requiring 16,000 parts for its solution, whereas it dissolves in 800 parts of boiling water. It separates from a filtered hot solution in water and from saline solutions in the red form, which then passes very slowly into the stable yellow modification.[2] It is less soluble in a solution of potassium iodide, in alcohol, and in dilute acetic acid than in water itself. It is not decomposed by dilute sulphuric acid, hydrochloric acid, or caustic potash. Nitric acid, however, decomposes it with evolution of iodine.

Thallous Chlorate, $TlClO_3$.—This salt is formed by mixing equivalent quantities of thallium sulphate and barium chlorate, filtering and concentrating the solution; the salt then separates out in microscopic prisms sparingly soluble in cold water (Thorpe).

Thallous Perchlorate, $TlClO_4$, is formed by dissolving thallium in aqueous perchloric acid, or by precipitating barium perchlorate

[1] Gernez, *Compt. rend.*, 1904, **138**, 1695.
[2] *Compt. rend.*, 1904, **139**, 278.

with thallous sulphate. It crystallises in transparent rhombic tablets, isomorphous with potassium perchlorate, and having a specific gravity of 4·844 at 15·5°. One part of this salt dissolves at 15° in 10 parts, and at 100° in 0·06 part of water; it is only slightly soluble in alcohol (Roscoe).

Thallium Monosulphide or *Thallous Sulphide*, Tl_2S, is a black precipitate formed when sulphuretted hydrogen is passed into an alkaline or acetic acid solution of a thallous salt. If the solution contains a trace of free sulphuric acid the sulphide separates out in the cold in microscopic tetrahedra (Hebberling). If the sulphide or a mixture of the metal with sulphur is melted in absence of air, a black glittering mass is obtained on cooling, having a specific gravity of about 8 and a general appearance somewhat like graphite. It is insoluble in water, alkalis, ammonium sulphide, and potassium cyanide. When the sulphide is heated to 150–200° with colourless ammonium sulphide it crystallises in long needles of metallic appearance, or in thin six-sided plates.[1] It dissolves with difficulty in acetic acid, but readily in mineral acids. The precipitated sulphide oxidises on exposure with formation of sulphate, and when heated in a current of hydrogen is reduced to thallium. Black lustrous prisms of a compound, Tl_2S_5, which is probably *thallous pentasulphide*, are obtained by the action of a solution of ammonium polysulphide on thallous chloride.[2]

Normal Thallous Sulphate, Tl_2SO_4.—This salt crystallises in rhombic prisms isomorphous with potassium sulphate and has a specific gravity of 6·6. 100 parts of water dissolve, according to Lamy, as follows:

At	18°	62°	101°
Tl_2SO_4	4·8	11·5	19·3.

It is much more soluble in dilute sulphuric acid than in water,[3] and melts at a red heat, decomposing in the presence of air with evolution of sulphur dioxide.

Thallous sulphate readily combines with other sulphates to form double salts such as $Tl_2SO_4,MgSO_4,6H_2O$, isomorphous with the analogous potassium compounds. It can also replace the alkali sulphates in the alums. Thus thallium alum, $Tl_2SO_4,Al_2(SO_4)_3,24H_2O$, crystallises in bright octahedra. Thal-

[1] Stanek, *Zeit. anorg. Chem.*, 1898, **17**, 117.
[2] Hofmann and Höchtlen, *Ber.*, 1903, **36**, 3090.
[3] Stortenbeker, *Rec. trav. chim.*, 1902, **21**, 87.

lium iron alum and thallium chromium alum have also been prepared.

Hydrogen Thallous Sulphate, $HTlSO_4,3H_2O$, crystallises in short thick prisms, which melt on heating, and then suddenly decompose into the normal sulphate with evolution of vapours of sulphuric acid. The anhydrous compound melts at 115–120°. A compound of the formula Tl_2SO_4, $TlHSO_4$ has also been described (Stortenbeker).

Thallous Nitrate, $TlNO_3$.—Nitric acid attacks thallium more easily than any other acid. Thallium nitrate crystallises in opaque, white rhombic prisms, having a specific gravity of 5·55; these pass at 72·8° into a rhombohedral form and at 142·5° into a regular modification.[1] The crystals melt at 206·1°, and the fused mass solidifies on cooling to a glass-like solid. It decomposes rapidly at 450°, leaving a residue of thallic oxide.[2] 100 parts of water dissolve, according to Lamy:

At	18°	58°	107°
$TlNO_3$	10·67	43·48	588·2.

It is insoluble in alcohol.

Phosphates of Thallium.—These salts are isomorphous with the analogous potassium compounds.

Normal Thallous Orthophosphate, Tl_3PO_4, is obtained in the form of needle-shaped crystals by precipitating the corresponding potassium salt with a thallium salt. It is also formed by the precipitation of ordinary sodium phosphate, but this precipitation is not complete (Lamy). One part dissolves at 15° in 201, and at 100° in 149 parts of water (Crookes). It is easily soluble in ammoniacal salts.

Monohydrogen Thallous Orthophosphate, HTl_2PO_4,H_2O, is formed by neutralising a boiling solution of phosphoric acid with thallium carbonate. When evaporated to a syrup, the concentrated solution deposits rhombic crystals. These lose their water at 200°, and when they are heated to dull redness a glassy mass of pyrophosphate remains behind.

Dihydrogen Thallous Orthophosphate, H_2TlPO_4.—This salt is obtained when phosphoric acid is added to a solution of the foregoing salt until the liquid exhibits a distinctly acid reaction. It crystallises in monoclinic pearly tablets, dissolves readily

[1] van Eyk, *Proc. K. Akad. Wet. Amsterdam*, 1900, **2**, 1480; **3**, 98; *Zeit. physikal. Chem.*, 1905, **51**, 721.

[2] Thomas, *Compt. rend.*, 1904, **138**, 1697.

in water, and on ignition is converted into the glassy metaphosphate.

Normal Thallous Carbonate, Tl_2CO_3.—Thallium hydroxide readily absorbs carbon dioxide. Thus if the moistened metal is allowed to lie exposed to the air, it becomes covered with needle-shaped crystals of the carbonate. This salt crystallises from solution in water in glittering monoclinic prisms, which have a caustic metallic taste and an alkaline reaction. 100 parts of water dissolve, according to Lamy:

At	18°	62°	100·8°
Tl_2CO_3	5·23	12·85	22·40.

It is insoluble in alcohol. It fuses on heating and decomposes at a higher temperature with evolution of carbon dioxide.

Hydrogen Thallous Carbonate appears not to be known in the solid state.

Thallous Cyanide, TlCN.—This salt is obtained by mixing strong solutions of potassium cyanide and thallous nitrate (Crookes). It separates in glittering plates not very soluble in water. When heated it decrepitates and melts easily, volatilising when strongly heated on platinum foil without reduction and without acting on the platinum. It is readily soluble in potassium cyanide and forms crystalline double cyanides.

Silicate of Thallium.—A solution of the hydroxide when boiled with amorphous silica dissolves this substance, and when the solution is evaporated a crystalline mass, having the composition $Tl_6Si_{10}O_{23} = 3Tl_2O,10SiO_2$, and also containing water, separates out. When thallium oxide is fused with silica a yellow, strongly refracting glass is obtained, which is occasionally employed in place of lead silicate for optical glass.

THALLIC COMPOUNDS.

349 Thallic oxide, like alumina, acts as a weak base. The salts with colourless acids are colourless, and are as a rule hydrolysed to a considerable extent in aqueous solution, so that many of them decompose when their solutions are largely diluted, or heated, the hydrated oxide being deposited. They are reduced by metallic thallium to thallous salts and show a greater tendency than these to form complex salts.[1]

[1] See Spencer and Abegg, *Zeit. anorg. Chem.*, 1905, **44**, 379.

Thallium Trioxide, Tl_2O_3.—When molten thallium is plunged into oxygen it takes fire with formation of this oxide. At a red-heat this is, however, converted into the monoxide. It is also obtained by passing a current from a few Bunsen elements through acidulated water, the positive pole consisting of metallic thallium which then becomes covered with a black deposit of this oxide [1] (Wöhler):

$$Tl_2 + 3H_2O = Tl_2O_3 + 3H_2.$$

It is also deposited on a platinum anode as a coherent film when an acid solution of thallous sulphate containing a little acetone is electrolysed,[2] and this separation may be utilised for the gravimetric estimation of thallium.

Thallic oxide is also obtained when hydrogen peroxide is added to an alkaline solution of a thallous salt and the resulting precipitate washed with alcohol and ether and dried in vacuo. When cold solutions are employed the oxide is brown, has the sp. gr. 9·65, and is readily soluble in acids, whereas the oxide obtained from hot solutions is black, has the sp. gr. 10·19, and is only slowly attacked by acids.[3] The crystalline oxide obtained by heating the nitrate, however, has the sp. gr. 9·97.[4]

As usually prepared, the oxide forms a dark reddish powder which is insoluble in water and the alkalis.

Thallic Hydroxide, $Tl(OH)_3$.—If a hot solution of thallous chloride in sodium carbonate is mixed with one of sodium hypochlorite, a brown precipitate is obtained which probably consists of amorphous thallic hydroxide, but on drying has the composition TlO(OH). The latter compound is also formed by the action of an alkali on thallic chloride. When treated with hydrochloric acid it evolves chlorine with formation of a thallous salt, whereas oxygen is given off when it is heated with concentrated sulphuric acid; on heating it is transformed into the trioxide and afterwards into the monoxide. If thallic oxide is fused for some time with potash containing a little water, thallic hydroxide, $Tl(OH)_3$, is left on treating the mass with water in the form of brown hexagonal plates, which are unaffected at a temperature of 340°.[5]

It was at one time supposed that thallic oxide was capable of

[1] *Annalen*, 1868, **146**, 243, 375.
[2] Heiberg, *Zeit. anorg. Chem.*, 1903, **35**, 347.
[3] Rabe, *Zeit. anorg. Chem.*, 1906, **48**, 427.
[4] Thomas, *Compt. rend.*, 1904, **138**, 1697.
[5] Carnegie, *Chem. News*, 1889, **60**, 113.

uniting with strong bases to form thallates, as it was observed that when thallic hydroxide was suspended in caustic potash and a current of chlorine passed in, a deep reddish-violet solution was formed. It was, however, found that the coloration was caused by the presence of a trace of manganese in the thallic hydroxide employed.

Thallic Chloride, $TlCl_3$, is formed when the monochloride is treated with chlorine under water. If the solution is evaporated at 60–70° and then cooled, deliquescent, colourless crystals of the hydrate $TlCl_3,4H_2O$ are obtained, which pass slowly in vacuo at the ordinary temperature, more rapidly at 55°, into the monohydrate. The anhydrous chloride can be obtained, according to Thomas, by direct dehydration of the tetrahydrate over caustic soda in vacuo, or according to Meyer by the decomposition in vacuo of the compound $TlCl_3,(C_2H_5)_2O$ obtained by the action of ether on the tetrahydrate. It forms a hard mass consisting of six-sided crystals, and melts at 24°.[1]

When thallium is strongly heated in chlorine a yellowish-brown mass of the composition $TlCl_3,3TlCl$ is formed, and this can also be obtained by the partial reduction of thallic chloride and by saturating a solution of this chloride with thallous chloride. It is sparingly soluble in cold, but readily in hot water, separating from this solution in dark-yellow six-sided tablets, strongly resembling lead iodide in appearance. Many compounds intermediate in composition between this and the trichloride have been described, but according to Meyer,[2] these are probably solid solutions of thallous chloride in thallic chloride, a continuous series being possible up to the limit of composition represented by $TlCl_3,3TlCl$.

When the metal is treated with nitrosyl chloride the compound $TlCl,TlCl_3,2NOCl$ is formed. If an alcoholic solution of the trichloride is heated with alcoholic ammonia, a white crystalline precipitate of $(NH_3)_3TlCl_3$ separates out; this is decomposed on contact with water with formation of the violet-coloured trioxide:

$$2(NH_3)_3TlCl_3 + 3H_2O = Tl_2O_3 + 6NH_4Cl.$$

The chloride also forms double salts with the chlorides of ammonium and potassium.

[1] Meyer, *Zeit. anorg. Chem.*, 1900, **24**, 321; Thomas, *Compt. rend.*, 1902, **135**, 1051. Compare McClenahan, *Amer. J. Sci.*, 1904, (4), **18**, 104.

[2] See also Cushman, *Amer. Chem. J.*, 1900, **24**, 222; Thomas, *Compt. rend.*, 1906, **142**, 838.

Thallic Bromide has not been obtained in the anhydrous state, but the monohydrate, $TlBr_3,H_2O$, is known. Like the chloride it unites with the corresponding thallous salt, but forms two definite compounds, $TlBr_3,TlBr$ and $TlBr_3,3TlBr$, as well as a series of solid solutions, all crystallising in plates.

A large number of chlorobromides have been described, which are obtained by the action of bromine on the chloride and of chlorine on the bromide, as well as by reactions between the chlorides and bromides themselves.[1]

Thallic Sulphide, Tl_2S_3, is formed when the metal is fused with an excess of sulphur. It is a black amorphous mass which at a summer temperature is soft and plastic like pitch. Below 12° it is hard and brittle, exhibiting a glassy fracture.

If one part of thallium sulphate is fused with 6 parts of sulphur and 6 parts of potassium carbonate, and the mass treated with water, a red crystalline powder remains behind having the composition $KTlS_2$. This substance is not attacked by caustic potash, but decomposes in presence of acids.

Thallic Sulphate, $Tl_2(SO_4)_3$, crystallises on evaporation of a solution of the trioxide in warm dilute sulphuric acid in the form of thin colourless tablets containing $7H_2O$, which are decomposed by water with separation of the hydrated trioxide.

It very readily forms the basic salt, $Tl(OH)(SO_4),2H_2O$, even in presence of sulphuric acid (Marshall), and yields the acid salt, $Tl_2(SO_4)_3,H_2SO_4,8H_2O$, when an excess of acid is present. This acid salt is decomposed at 220°, leaving the anhydrous sulphate (Meyer and Goldschmidt).

No true alums have as yet been prepared containing thallic sulphate in place of aluminium sulphate, but salts of the type $M_2SO_4,Tl_2(SO_4)_3,8H_2O$ have been prepared containing the sulphates of ammonium, potassium, and rubidium. Crystals of ammonium alum have, however, been obtained containing variable amounts of thallic sulphate, and it seems probable, therefore, that thallic sulphate, like the sulphates of aluminium, gallium, and indium, is capable of forming true alums.[2]

A number of complex thallo-thallic sulphates have been described. The simplest of these has the composition $Tl_2SO_4,Tl_2(SO_4)_3$, and is formed when equivalent amounts of

[1] Meyer, *Zeit. anorg. Chem.*, 1900, **24**, 321; Cushman, *Amer. Chem. J.*, 1900, **24**, 222; Thomas, *Compt. rend.*, 1900, **131**, 892, 1208; 1901, **132**, 80, 1487; 1901, **133**, 735; 1902, **134**, 545; 1902, **135**, 1051.

[2] Piccini and Fortini, *Zeit. anorg. Chem.*, 1902, **31**, 451.

thallous and thallic sulphate are dissolved in water and the solution allowed to crystallise.[1]

Thallic Nitrate, $Tl(NO_3)_3,3H_2O$, is deposited from a solution of the oxide in nitric acid in colourless deliquescent crystals, which decompose on heating with water.

The complex salt, $2TlNO_3,Tl(NO_3)_3$, crystallises in prisms, melts at 150°, and is decomposed by moist air.[2]

Detection and Estimation of Thallium.

350 The salts of thallium are poisonous, and the soluble salts possess a disagreeable metallic taste. Their presence may be readily detected by the beautiful green colour which they impart to a non-luminous gas-flame. The spectrum of this flame consists of one bright green line having a wave-length of 5351, not coincident with any line in the solar spectrum. Thallium may be readily separated from all the other metals by treating an acid solution with sulphuretted hydrogen, filtering off the separated sulphides, and precipitating the filtrate with sulphide of ammonium, which throws down thallium sulphide as a black precipitate. This precipitate may contain also the sulphides and hydroxides of the metals of the iron group; to separate these, it is washed, dissolved in nitric acid, and the boiling solution neutralised with sodium carbonate; on cooling, chloroplatinic acid is added, when a pale yellow precipitate of the double chloride of thallium and platinum, $2TlCl,PtCl_4$, is thrown down. This compound dissolves in 15,600 parts of cold water, and hence may be employed for the quantitative estimation of thallium. Thallium may also be precipitated by potassium iodide as thallium iodide, which in presence of an alkali iodide is altogether insoluble in water.

Several other methods for the estimation of thallium have been proposed, based on the oxidation of thallous to thallic salts, by means of bromine, iodine, or auric bromide.[3] As already mentioned, thallium may also be estimated by the electrolytic deposition of thallic oxide. It can also be estimated as metal by using a mercury cathode and a rotating anode. The salts

[1] Lepsius, *Chem. Centr.*, 1891, i., 694. See also Marshall, *Proc. Roy. Soc. Edin.*, 1902, **24**, 305; Meyer and Goldschmidt, *Ber.*, 1903, **36**, 238.

[2] *Amer. Chem. J.*, 1901, **26**, 275.

[3] Marshall, *J. Soc. Chem. Ind.*, 1900, **19**, 994; Thomas, *Compt. rend.*, 1900, **130**, 1316; 1902, **134**, 655.

derived from volatile acids may be converted into sulphate by careful heating with sulphuric acid, and the thallium weighed in this form. Finally, thallic salts may be precipitated in neutral solution by ammonia, the liquid boiled, and the resulting thallic oxide dried at 60—70° and weighed.

The Atomic Weight of thallium has been determined by Crookes[1] by converting the metal into the nitrate. Ten experiments gave numbers lying between 202·62 and 202·65 (H = 1). The corresponding number 204·1 (O = 16) has been confirmed by Lepierre, who analysed thallic oxide and thallous sulphate, and determined the amount of thallic oxide which could be obtained from a thallous salt.[2] The number accepted now (1913) is 204·0.

[1] *Phil. Trans.*, 1873, **163**, 277. [2] *Compt. rend.*, 1893, **116**, 580.

METALS OF THE RARE EARTHS.

Scandium, Sc	Cerium, Ce	Erbium, Er
Yttrium, Yt	Dysprosium, Dy	Holmium, Ho
Lanthanum, La	Europium, Eu	Thulium, Tm
	Gadolinium, Gd	
	Neodymium, Nd	
	Praseodymium, Pr	
	Samarium, Sa	
	Terbium, Tb	
	Neo-ytterbium, Yb	
	Lutecium, Lu	
	Celtium, Ct	

351 The three metals of the boron group are also members of the very extensive class of elements known as the metals of the rare earths. The names of these are given above in three groups, the first of which comprises the three metals which with boron make up sub-group *a* of group III.; the second, those of which the individuality is at least probable; the third, those which are probably mixtures of greater or less complexity. The relation of these elements to the periodic system of classification has given rise to much discussion (p. 69), and opinions are still divided as to whether they form an anomalous group occupying a single position in the periodic system, or whether they are to be assigned to the vacant spaces in series 8, 9, 10 (pp. 50–51).[1]

Cerium, although it possibly belongs to group IV., is so closely allied to the other metals of the rare earths in many of its properties that it is included among them, and the whole group is described together with scandium, yttrium and

[1] See Werner, *Ber.*, 1905, **38**, 914; Armstrong, *Proc. Roy. Soc.*, 1902, **70**, 86; Brauner, *J. Russ. Chem. Phys. Soc.*, 1902, **34**, 142; *Zeit. Elektrochem.*, 1906, 17; Biltz, *Ber.*, 1902, **35**, 562; Brauner, *Zeit. Elektrochem.*, 1908, 525.

lanthanum, with which its members occur and which they closely resemble in properties.[1]

The earths formerly described as philippia and mosandria have been proved to be mixtures of other earths,[2] and it is probable that the compounds of decipium (Delafontaine)[3] and victorium (Crookes)[4] are also mixtures.

352 In the year 1794 Professor Gadolin, of Abo, in Finland, discovered a new earth in the mineral, termed after him gadolinite, which had been found at Ytterby in the year 1788. This discovery was confirmed in the year 1797 by Eckeberg, who found that the compound separated by Gadolin contained, together with glucina, a new earth, to which he gave the name of yttria. In 1803 Klaproth discovered a second peculiar earth in another Swedish mineral found at Riddarhyttan, which mineral had formerly been supposed to contain tungsten, and to this, because it became dark-yellow on heating, he gave the name of ochroite. The same substance was examined simultaneously by Berzelius and Hisinger, who considered it as the oxide of a new metal which they termed cerium, after the planet Ceres, which had been recently discovered, whilst the mineral was called cerite.

In 1819 Berzelius observed that crude yttria also contained ceria; and Mosander, in 1839, showed, in a most careful investigation, that ceria contained the oxide of another metal, to which he gave the name of lanthanum (*λανθάνω*, I lie hidden). In 1841 he discovered that the latter was not pure, but contained a third new element, to which he gave the name didymium (from *διδύμοι*, twins). The same chemist in 1843 concluded from another series of investigations that yttrium was invariably accompanied by two other metals, to which he gave the names of terbium and erbium from the terminal letters of the stem of the word Ytterby. According to the investigations of Bunsen and Bahr,[5] only one of the last two metals appeared

[1] An elaborate monograph on the Rare Earths by R. J. Meyer, with a very full discussion of their atomic weights by Brauner, is contained in Abegg's *Handbuch der anorganischen Chemie*, vol. iii., part I. (Hirzel, Leipzig, 1906). A short article contributed by Brauner to Mendeléeff's *Principles of Chemistry*, Vol. II., pp. 105–124 (Longmans, London, 1905), Böhm's *Darstellung der Seltnen Erden*, 2 vols. (Veit & Co., Leipzig, 1905), and R. J. Meyer and O. Hauser's *Die Analyse der seltenen Erden und der Erdsaüren* (F. Enke, Stuttgart, 1912), also contain much valuable information on the subject.

[2] See Roscoe, *Ber.*, 1882, **15**, 1274. [3] *Compt. rend.*, 1881, **93**, 63.

[4] *Proc. Roy. Soc.*, 1899, **65**, 237; Urbain, *Compt. rend.*, 1905, **141**, 954.

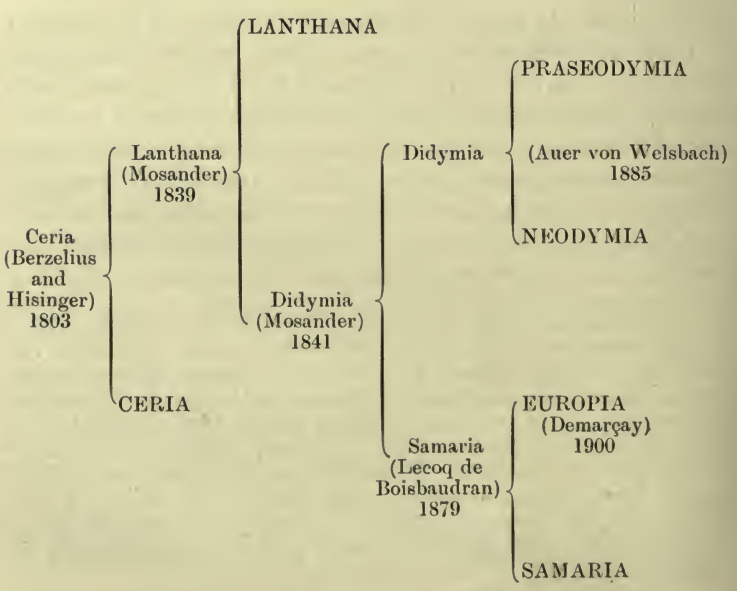
[5] *Annalen*, 1866, **137**, 1.

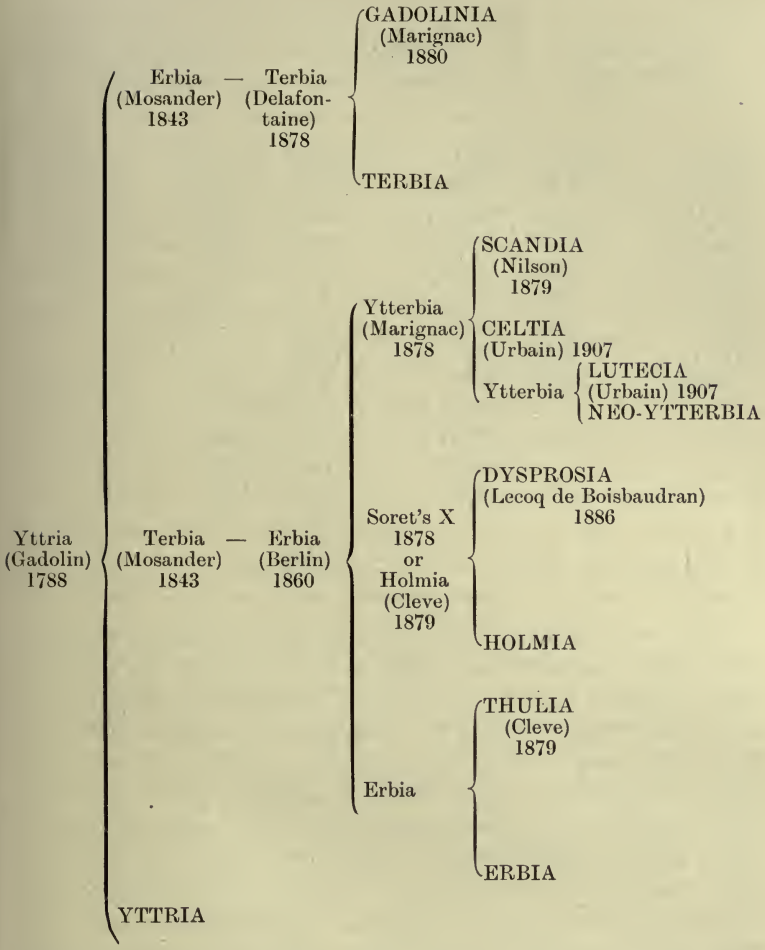
to exist, and for this they retained the name erbium, but the subsequent researches of Delafontaine and Marignac showed that both elements were present.

Further investigations have proved that the substances which all these chemists examined were in most cases highly complex mixtures, the complete separation of which has not yet been effected. This is illustrated by the two following tables which show the earths which have so far been obtained from yttria and ceria. The name of the investigator who effected each separation is added together with the date. Further details will be found under the headings of the separate metals.

Europia has also been found as a constituent of Delafontaine's terbia, and of both of the earths obtained from it by Marignac.

353 The rare earths occur in several rare minerals found in various localities in Scandinavia, Siberia, Greenland, North America, and Brazil. They are usually present in the form of silicates, less frequently as columbates, tantalates, phosphates, fluorides, and uranates, and are often accompanied by the oxides of glucinum and zirconium. The most important of these minerals are *gadolinite*, a basic orthosilicate of glucinum, iron, and the yttrium metals; *cerite*, a hydrated silicate of calcium and the cerium metals; *keilhauite*, a titanosilicate of yttrium, aluminium, iron, and calcium; *samarskite*, a columbate and





tantalate of iron, calcium, uranyl, and the metals of both the cerium and yttrium groups; *fergusonite*, a columbate of both the yttrium and cerium metals; *euxenite*, a columbate and titanate of yttrium, cerium, erbium, and uranyl; *monazite*, an orthophosphate of the cerite earths containing thorium; *xenotime*, an orthophosphate of the yttrium metals; and *thorianite*, a mineral found in Ceylon, containing 70 per cent. of thoria together with the oxides of uranium, cerium, lanthanum, didymium, yttrium, and zirconium.[1] The subjoined analyses[2] give some idea of the general composition of three of these minerals.

[1] Dunstan and Blake, *Proc. Roy. Soc.*, 1905, **76**, 253.

[2] Quoted from Dana's *Mineralogy* (1892).

Cerite. (Lindström, 1873).		Gadolinite from Ytterby. (Pettersson, 1890).		Samarskite from N. Carolina. (Allen, 1877).	
SiO_2	22·79	SiO_2	23·88	Ta_2O_5	18·20
Ce_2O_3	24·06	ThO_2	0·41	Cb_2O_5	37·50
Di_2O_3, La_2O_3	35·37	Yt_2O_3	45·30	SnO_2, WO_2	0·08
FeO	3·92	Ce_2O_3	3·84	UO_3	12·54
Al_2O_3	1·26	Di_2O_3, La_2O_3	2·57	Ce_2O_3, Di_2O_3, La_2O_3	4·17
CaO	4·35	Fe_2O_3	0·60	Yt_2O_3	14·48
H_2O	3·44	FeO	12·89	FeO	10·75
Gangue	4·33	GlO	9·91	MnO	0·78
	99·52	CaO, MgO	0·54	CaO	0·55
		Na_2O	0·15	H_2O	1·12
		H_2O	0·57		100·17
			100·66		

The crude earths are obtained from the minerals by methods which differ somewhat according to the nature of the material to be treated. Cerite is evaporated with strong sulphuric acid, the excess of acid removed by heating, and the residue dissolved in ice-cold water. The clear solution is saturated with sulphuretted hydrogen, again filtered, and then made acid with hydrochloric acid and precipitated with oxalic acid, by means of which the insoluble oxalates of the earths, consisting mainly of ceria, lanthana, and didymia, are obtained and are finally converted into the oxides by ignition. Gadolinite, on the other hand, is decomposed by hydrochloric acid, and the oxalates then precipitated from the solution of the chlorides. In other cases (fergusonite) the mineral is fused with potassium bisulphate, the fused mass is extracted with water, and the earths are precipitated as hydroxides or oxalates.

The nature of the crude oxide thus obtained varies very greatly according to the source from which it is derived. The different earths, with but few exceptions, resemble one another very closely, so that, in order to separate them, advantage has to be taken of very slight differences in chemical behaviour, and the processes of separation are repeated a very large number, often amounting to many hundreds, of times It is therefore advisable to commence the preparation of any par-

ticular earth with a mineral which contains it in as large a proportion and as free from admixture as possible, since in this way the length and tediousness of the processes of separation are lessened.

In some cases it is advisable first of all to remove the cerium, especially when this element is present in large proportion. This may be effected by a number of different methods, all of which depend on the fact that when the oxalates are calcined cerium forms an oxide, CeO_2, and that the derivatives of this differ very considerably from those of the oxides of the type R_2O_3 formed by the other earths. Of these methods one of the most effective is to convert the oxides into nitrates and pour a solution of these into a large amount of boiling water, under which circumstances a basic ceric nitrate separates, containing only a small amount of praseodymium and neodymium, from which it can be freed by several repetitions of the process. A second method is to add a solution of some salt of the earths to potassium permanganate solution containing magnesia in suspension. Ceric hydroxide is precipitated, and the filtrate is free from cerium (R. J. Meyer and Schweitzer).

A rough division of the mixed earths into two groups is obtained by saturating the neutral solution of the crude oxide in nitric acid with potassium sulphate. Double salts are formed of the general formula $R_2(SO_4)_3,3K_2SO_4$, those of the yttrium group (Yt, Yb, Lu, Er, Ho, Tm, Tb, Sc) being soluble, whilst those of the cerium group (Nd, Pr, La, Ce, Sa Gd) are insoluble in a saturated solution of potassium sulphate. The sulphates thus obtained may be converted into oxalates, which are only sparingly soluble in dilute acids, or into oxides, and the separation repeated as often as is desired. For the further separation of the oxides which have been submitted to the foregoing treatment a number of different methods have been proposed, which may be grouped under the following four heads.[1]

(1) *Ignition of the Nitrates* (Bahr and Bunsen).—When the neutral nitrates of the earths of either of these groups are gently heated, it is found that the salts of the different earths are decomposed at different temperatures. In the case of the yttrium group of oxides, to which the method is best applied, the nitrates decompose in the following order, Sc, Yb, Er, Ho, Tm, Tb, Yt, yttrium nitrate requiring the highest temperature.

[1] Compare Losse, *Zeit. anorg. Chem.*, 1892, **3**, 56.

The heating is therefore continued only until a slight amount of decomposition has taken place; the cooled mass is then extracted with boiling water, and the basic salt which separates on cooling is removed by filtration. The filtrate is then evaporated and the process repeated.

(2) *Fractional Precipitation with Ammonia or some other Base.*—The neutral nitrate obtained from the crude earth is dissolved in water and ammonia added in such quantity as only to precipitate a portion of the earths which are present, the solution being so dilute that the precipitation takes place slowly. In this way the least basic earths are first precipitated, whilst the most basic are found in the filtrate. Among the cerium group of earths, lanthana appears to be the most basic, and is followed by ceria, praseodymia, neodymia, samaria, and gadolinia. The precipitated hydroxide is filtered off, redissolved in nitric acid, and again submitted to fractional precipitation, whilst the filtrate is treated in a similar manner to the original solution. Other bases, such as caustic potash, magnesia, or the weak organic base aniline, may be employed in a similar manner.

(3) *Fractional Crystallisation of Salts.*—This method has been applied to a very large number of different salts, and has proved of the greatest value for the separation of many of the rare earths. The most important results have been attained by the crystallisation of the double ammonium nitrates (praseodymium and neodymium), the double magnesium nitrates (europium), and the double potassium sulphates (samarium, scandium), but the formates,[1] carbonates, oxalates, ethyl sulphates,[2] and aceto-acetates have all been employed. The crystallisation of the double magnesium nitrates of the earths of the terbium group with the addition of bismuth nitrate has led to the isolation of pure salts of gadolinium and terbium (Urbain and Lacombe).

James[3] effects a separation of the yttrium earths by crystallisation of the bromates, the order of separation of the rare earth bromates from aqueous solution being samaria, europia, gadolinia, terbia, yttria, dysprosia, holmia, erbia, thulia, and ytterbia. In this way pure thulia and yttria can be obtained.

(4) *Fractional Precipitation of Salts.*—Lehner and Benner[4]

[1] Urbain, *Compt. rend.*, 1906, **142**, 785.

[2] Bettendorf, *Annalen*, 1907, **352**, 88.

[3] James, *Chem. News*, 1907, **75**, 181; 1908, **97**, 61, 205; *J. Amer. Chem. Soc.*, 1912, **34**, 757.

[4] *J. Amer. Chem. Soc.*, 1908, **30**, 572; 1911, **33**, 50.

effect a separation of the yttrium earths by fractional precipitation of a hot solution of the nitrates with sodium succinate. The earths precipitated first are holmia, terbia, and europia, whilst the major portion of the yttria is left in the solution. When a hot alcoholic solution of sodium stearate is added cautiously to a hot solution of the nitrates of the yttria earths a rapid separation can be effected (Stoddart and Hill).[1] The gadolinia and ceria earths can also be separated by this method.

354 The progress of the separation effected by any of these means may be followed by several methods, one of the most reliable of which is the determination of the chemical equivalent of the oxide obtained. This is accomplished by precipitating the earth in the form of oxalate, igniting, and weighing the oxide; this is then exposed to steam and afterwards evaporated with dilute sulphuric acid and heated gently over a small flame, or, better, at the temperature of sulphur vapour, until the weight is constant. The amount of sulphate formed from a known weight of oxide is thus ascertained, from which the equivalent of the earth can be calculated. This method is of great value when the earths which are being separated differ considerably in their equivalents, but is, of course, less useful when, as is often the case, the mixture consists of earths which have nearly the same equivalent.

The other methods employed for detecting the progress of purification or separation are all applications of spectrum analysis. In addition to the spark spectra, or those shown in the electric arc, the salts of many of the earths in solution exhibit characteristic absorption spectra. A number of the earths, moreover, show "phosphorescence spectra" when the ignited earth or its basic sulphate is exposed to an electric discharge in a highly exhausted glass bulb (Crookes), or exhibit a characteristic spectrum when an induction spark is made to pass from a positive pole of platinum on to the centre of the surface of a solution of one of the salts of the earth, which is connected with the negative pole (reversion spectra of Lecoq de Boisbaudran).

The evidence afforded by the study of the spectra yielded by the earths in any of these ways is very difficult to interpret because we are at present unacquainted with the exact influence of many variable conditions, especially the presence of other substances, upon the phenomena in question, and this

[1] *J. Amer. Chem. Soc.*, 1911, **33**, 1076.

influence is of very great importance, especially as regards absorption spectra and phosphorescence spectra. Krüss and Nilson,[1] arguing from the variation in the absorption spectra of the nitrates of the rare earths, and Crookes,[2] from a study of phosphorescence spectra, came independently to the conclusion that a very large number (24–30) of different elements were present in the rare earths. The chemical evidence, so far as it has been obtained, has not confirmed these views. The further study of absorption spectra, moreover, has shown that variations in the intensity and position of the bands may be produced by many factors and do not therefore necessarily indicate changes of composition. As regards phosphorescence spectra it has been shown that pure earths do not yield a discontinuous phosphorescence spectrum, but that such a spectrum is produced in the presence of small amounts of other substances and varies both with the amount and nature of this second substance.[3]

355 The metals of this group were at first supposed to be divalent, the general formula of the earths being written RO. In 1870 Mendeléeff found that whilst the equivalent of cerium was 46·3, its specific heat was about 0·05, whilst Hillebrand obtained the more accurate number 0·04479. According to this the atomic weight of cerium must be 139 and not 92·6 as previously supposed, since $139 \times 0{\cdot}04479 = 6{\cdot}3$, the lower basic oxide being therefore Ce_2O_3, and the higher oxide CeO_2.

It was suggested at the same time that the basic oxides of didymium and lanthanum, which had nearly the same equivalent as cerium, might be Di_2O_3 and LaO_2, didymium (138) being placed in the third group of the periodic system, and lanthanum, with an atomic weight of about 180, in the fourth group along with cerium. In this way these metals found a place in the periodic system, whilst no place existed for them in that system if their atomic weights were taken as about 92. The atomic weight of yttrium, the compounds of which were then but little known, was at the same time altered for similar reasons from about 59 to 88, the oxide being formulated Yt_2O_3 instead of YtO, and the metal placed in the third group of the periodic system.

The subsequent determination of the specific heats of lanthanum (0·04485) and the old didymium (0·04563) by Hillebrand showed that both these metals had an atomic weight of about

[1] *Ber.*, 1887, **20**, 2170. [2] See *Journ. Chem. Soc.*, 1889, **55**, 260.
[3] Baur and Marc, *Ber.*, 1901, **34**, 2460.

140, and a more accurate determination of their equivalents led to the atomic values La = 137·5, Di = 144. Oxide of lanthanum was, therefore, formulated La_2O_3 and the metal placed in the third group. The salts of didymium have since that date been shown to consist of the salts of at least two distinct elements, and the relations of these to the other elements have not yet been satisfactorily decided.

At present the general formula R_2O_3 is applied to the basic oxides of all the rare earth metals, and the formulæ of their salts are written in accordance with this.

SCANDIUM. Sc = 44·1.

356 The oxide of this metal, which has not itself been isolated, was discovered in euxenite in 1879 by Nilson,[1] who obtained 2 grams of the pure oxide from 10 kilos. of the mineral. The element scandium is of very wide occurrence,[2] but only in very small quantities. The minerals wiikite and an orthite from Finland are the richest,[3] and both contain less than one per cent. of the oxide. It is less basic than any of the other rare earths.

Scandium occupies the place in the periodic system which was assigned by Mendeléeff in 1869 to the unknown element ekaboron (p. 68). Speaking of this undiscovered element he said in the course of a full discussion of the subject[4]: Its atomic weight will be about 44, and its oxide, Ek_2O_3, will be a stronger base than alumina and will have a specific gravity of about 3·5, whilst the specific gravity of the chloride will be about 2. The oxide will be insoluble in alkalis and the salts colourless, yielding gelatinous precipitates with potash, potassium carbonate, sodium phosphate, etc.

Scandia is obtained from the mixed oxides of the rare earths either by precipitating as fluoride and further purification by the usual methods, or by precipitating as silicofluoride. The most persistent impurity is thoria and this is

[1] *Ber.*, 1879, **12**, 554; 1880, **13**, 1439.

[2] Ebethard, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 851; 1910, 404; Crookes, *Proc. Roy. Soc.*, 1908, **80**, A, 516; Vernadsky, *Bull. Acad. Sci. St. Petersburg*, 1908, 1273.

[3] Meyer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 379.

[4] *Annalen Supplementband*, 1872, **8**, 197.

removed[1] by treatment with sodium thiosulphate, when the scandium is precipitated and the major part of the thorium left in solution. The last traces of thoria are removed[2] by adding excess of potassium iodate to a nitric acid solution of the nitrate, when the thoria is precipitated as iodate.

Scandium Hydroxide, $Sc(OH)_3$, is a gelatinous white precipitate which on ignition yields the *oxide*, Sc_2O_3. The latter is a white powder resembling magnesia, of specific gravity 3·864. The salts are colourless and exhibit no absorption bands. The chloride[3] and bromide, Sc_2Cl_6 and Sc_2Br_6, crystallise with $12H_2O$; the fluoride is anhydrous. The *sulphate*, $Sc_2(SO_4)_3$, crystallises with $6H_2O$ and is readily soluble in water, differing in these respects from the other sulphates of the group. The double sulphate of scandium and potassium, $Sc_2(SO_4)_3,3K_2SO_4$, is insoluble in a solution of potassium sulphate. The nitrate,[3] $Sc(NO_3)_3,4H_2O$, forms prismatic crystals and becomes anhydrous when heated on the water-bath. When heated in a vacuum at 100° a basic nitrate, $Sc(OH)(NO_3)_2$, is formed. The borate, iodate, aurichloride, platinocyanide, and numerous salts of organic acids have been prepared.[3] The spark spectrum of the chloride is characteristic (Thalén). The arc spectrum has been mapped by Lockyer and Baxandall[4] and compared with the solar spectrum, in which many of the scandium lines are to be found.

YTTRIUM. Yt = 89·0

357 Yttria is the most basic of all the yttrium group of earths and its separation from the others is based on this fact. According to Crookes it is a complicated mixture,[5] but this conclusion has not been confirmed (p. 780).

Yttrium was obtained by Cleve as a dark-grey powder possessing a metallic lustre under the burnisher. He prepared it by the electrolysis of the double chloride of yttrium and sodium, and also by fusing this salt with sodium. Yttrium decomposes water slowly in the cold but more quickly on boiling.[6]

[1] Meyer, *Zeit. anorg. Chem.*, 1908, **60**, 134; Meyer and Winter, *ibid.*, 1910, **67**, 398.

[2] Meyer, *Chem. News*, 1912, **106**, 13.

[3] Crookes, *Phil. Trans.*, 1908, **209**, A., 15; *ibid.*, 1910, **210**, A., 359.

[4] *Proc. Roy. Soc.*, 1905, **74**, 538. [5] *Journ. Chem. Soc.*, 1889, **55**, 260.

[6] Cleve, *Compt. rend.*, 1882, **95**, 1125.

Yttrium Oxide, Yt_2O_3, is obtained as a white powder of sp. gr. 5·046 by igniting the oxalate or hydroxide. On ignition this emits a bright white light. It does not combine directly with water, but when an yttrium salt is precipitated with an alkali the *hydroxide* is thrown down as a gelatinous precipitate. Yttrium oxide dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids.

Yttrium Fluoride occurs together with the fluorides of cerium and calcium in the mineral yttrocerite found near Fahlun in Sweden, at Amity, Orange County, New York, in Massachusetts, and at Mount Mica in Maine. It is massive, crystalline-granular, and earthy, having a glistening vitreous to pearly lustre, and a colour varying from violet-blue to grey and white. Sometimes it has a reddish-brown colour.

Yttrium Chloride, $YtCl_3$, formed by heating the oxide mixed with carbon in chlorine, or more easily [1] by passing a mixture of dry chlorine, hydrogen chloride and sulphur chloride over the heated residue obtained by evaporation of a solution of the oxide in hydrochloric acid, is a colourless transparent substance. When the oxide is dissolved in hydrochloric acid the hydrate $YtCl_3,6H_2O$ is obtained on evaporation in deliquescent prisms which are soluble in alcohol but insoluble in ether. These decompose when heated alone with evolution of hydrogen chloride but when ignited in presence of sal-ammoniac or in a current of hydrogen chloride [2] the anhydrous chloride is obtained. The anhydrous chloride is soluble in pyridine, with which it forms an additive compound.[2] The hydrated chloride forms a compound, $YtCl_3,11H_2O,2C_6H_{12}N_4$, when treated with hexamethylene tetramine.[3]

The bromide and iodide are very similar to the chloride.

Yttrium Sulphide, Yt_2S_3, is obtained as a yellow or grey powder by heating the oxide in the vapour of carbon disulphide (Popp), and by heating the chloride in sulphuretted hydrogen. It is not soluble in water, but is decomposed by acids (Wöhler).

Yttrium Sulphate, $Yt_2(SO_4)_3,8H_2O$, forms transparent crystals which lose their water at 115°. 100 parts of cold water dissolve 9·3 parts of the salt, but when the solution is warmed to 100° 4·5 parts separate out in the crystalline state. It forms a

[1] Matignon, *Compt. rend.*, 1905, **140**, 1181.
[2] *Ann. Chim. Phys.*, 1906, [8], **8**, 433.
[3] Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1911, [v], **20**, i. 164.

microcrystalline powder with stannic sulphate[1] having the formula $YtSn(SO_4)_6$. On heating yttrium sulphate at 700° a basic sulphate, Yt_2O_3,SO_3, is formed, which crystallises in white needles.[2]

Yttrium Nitrate, $Yt(NO_3)_3,6H_2O$, is easily soluble in water, alcohol, and ether, forming large needles. At 25° 100 grams of water dissolve 141·6 grams of the nitrate. A basic nitrate[3] of the formula, $3Yt_2O_3,4N_2O_5,20H_2O$, is formed by shaking the oxide with nitric acid at 25°. This compound is stable in the presence of an aqueous solution of $Yt(NO_3)_3$ containing 33 grams per 100 c.c. The normal nitrate forms a compound with hexamethylene tetramine,[4] having the formula $Yt(NO_3)_3,10H_2O,2C_6H_{12}N_4$.

Yttrium Orthophosphate, $YtPO_4,2H_2O$, is slightly soluble in water; the *metaphosphate*, $Yt(PO_3)_3$, is an insoluble crystalline powder; and the *pyrophosphate*, $2YtHP_2O_7,7H_2O$, is soluble in water.

Yttrium Carbide, YtC_2, is prepared by heating the oxide with carbon in the electric furnace. It forms yellow microscopic crystals of sp. gr. 4·13, and yields with water a mixture of gases containing 72 per cent. of acetylene, along with methane, ethylene, and hydrogen.

Yttrium Carbonate, $Yt_2(CO_3)_3,3H_2O$, is a heavy white powder insoluble in water.

Yttrium Bromate,[5] $Yt_2(BrO_3)_6,18H_2O$, is a white crystalline substance forming hexagonal prisms. It is formed by the action of barium bromate on yttrium sulphate, and dissolves to the extent of 168 parts in 100 of water at 25°.

Detection and Estimation of Yttrium.

358 This metal is most readily recognised by the spark spectrum of the chloride. This contains a large number of bright lines, of which two groups lying near the sodium line towards the red are especially characteristic. The salts show no absorption spectrum. The reactions of the yttrium salts are very similar to those of zirconium.

The Atomic Weight of yttrium was determined by Bahr and Bunsen by the analysis of the sulphate to be 92. According to

[1] Weiland and Kuhl, *Zeit. anorg. Chem.*, 1907, **54**, 244.
[2] Brill, *Zeit. anorg. Chem.*, 1905, **47**, 464.
[3] James and Pratt, *J. Amer. Chem. Soc.*, 1910, **32**, 873.
[4] Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1911, [v], **20**, i., 164.
[5] James and Langelier, *J. Amer. Chem. Soc.*, 1909, **31**, 913.

Cleve and Hoeglund,[1] on the other hand, it is 89·2. This difference is probably due to the presence of other earths. From a still later determination[2] Cleve obtained the number 88·4, whilst the somewhat lower number 88·3 was obtained by Jones.[3] The number at present (1913) adopted is 89·0.

LANTHANUM. La = 139·0.

359 Lanthanum salts are best obtained pure by the fractional crystallisation of the double magnesium nitrates of the cerite earths.[4] Lanthana is the most basic of all the rare earths. *Lanthanum* was obtained by Mosander as a grey powder by heating the chloride with potassium. Hillebrand and Norton[5] prepared it by the electrolysis of the fused chloride, and obtained it in the form of fused globules, some of which weighed as much as six grams, and it has since been prepared in large quantities by the same method by Muthmann and Kraft.[6] Thus prepared it has a specific gravity of 6·154 and an iron-grey colour ; it takes a high polish but soon tarnishes, even on exposure to dry air, attaining a steel-blue colour. The metal can be hammered out to tolerably thin foil, and can be drawn into wire. The specific heat of the metal is 0·04485 and it melts at 810°. When heated in the air it forms oxide and nitride. The finely-divided metal burns brightly when thrown into the flame. It also takes fire when thrown into chlorine gas, burns less brightly in bromine vapour, and combines with iodine without evolution of light. Cold water oxidises it slowly with formation of the hydroxide. Cold concentrated sulphuric acid does not attack it, but in dilute sulphuric acid and in hydrochloric acid it dissolves with violent evolution of hydrogen, and it is oxidised by both concentrated and dilute nitric acid.

Lanthanum Oxide, La_2O_3.—This is obtained in the form of a white powder which has a specific gravity of 6·48, by heating the hydroxide, oxalate, carbonate, or nitrate. It combines with water with evolution of heat, like lime, with formation of a voluminous snow-white powder of *lanthanum hydroxide*, $La(OH)_3$;

[1] *Bull. Soc. chim.*, 1872, [2], **18**, 193. [2] *Ibid.*, 1883, [2], **39**, 120.
[3] *Amer. Chem. J.*, 1895, **17**, 154.
[4] Drossbach, *Ber.*, 1902, **35**, 2826; Muthmann and Weiss, *Annalen*, 1904, **331**, 1.
[5] *Pogg. Ann.*, 1875, **156**, 466. [6] *Annalen*, 1902, **325**, 261.

this is obtained also by precipitating a lanthanum salt with an alkali in the form of a gelatinous precipitate which easily absorbs carbon dioxide from the air. The hydroxide has an alkaline reaction and decomposes ammonium salts on heating.

The oxide is readily reduced when it is heated with magnesium powder. If the reaction is carried out in an atmosphere of hydrogen, a *hydride of lanthanum*, LaH_3, is formed [1] which has been prepared pure by heating the pure metal in hydrogen at about 240° (Muthmann and Kraft).

A *peroxide*, which appears to be a hydrated form of the oxide La_2O_5, is precipitated when hydrogen peroxide and an alkali are added to a solution of a lanthanum salt.

Lanthanum Chloride, $LaCl_3$.—This substance is obtained in the anhydrous state by heating its ammonium double salt, or by passing a mixture [2] of chlorine, hydrogen chloride and sulphur chloride over the heated hydrated chloride. It is a crystalline mass very soluble in water and alcohol, has a density [2] of 3·95, at 18° and melts at 907°. When the oxide is dissolved in hydrochloric acid, and the solution evaporated to a syrup, large prisms having the composition $2LaCl_3,15H_2O$ are deposited, and these when heated lose hydrogen chloride.

Lanthanum Sulphide, La_2S_3, is obtained by heating the oxide in the vapour of carbon disulphide, in the form of a yellow mass which is decomposed by water. A disulphide,[3] LaS_2, has been prepared by heating $La_2(SO_4)_3$ in sulphuretted hydrogen at 600°. It decomposes at 650° into the trisulphide, La_2S_3.

Lanthanum Sulphate, $La_2(SO_4)_3,9H_2O$, crystallises at the ordinary temperature in six-sided pointed prisms which are more soluble in cold than in hot water, whilst at 0° a hydrate with $16H_2O$ separates out (Brauner and Pavlicek). One part of the anhydrous salt dissolves at 3° in less than 6 parts, whilst at 100° it dissolves in about 115 parts of water. The double potassium salt is insoluble in a solution of potassium sulphate. With stannic sulphate [4] it forms a compound, $LaHSn(SO_4)_4$, which crystallises in six-sided plates. On heating the anhydrous sulphate at 700° a basic sulphate is formed [5] of the formula La_2O_3,SO_3, which forms white needles. The hydrated sulphate

[1] Winkler, *Ber.*, 1890, **23**, 787; 1891, **24**, 890.
[2] Matignon, *Compt. rend.*, 1905, **140**, 1339; 1181.
[3] Biltz, *Zeit. anorg. Chem.*, 1911, **71**, 427.
[4] Weinland and Kühl, *Zeit. anorg. Chem.*, 1907, **54**, 244.
[5] Brill, *Zeit. anorg. Chem.*, 1905, **47**, 464.

crystallises[1] with the sulphates of the alkalis and forms the compounds:

$$La_2(SO_4)_3,K_2SO_4,2H_2O;\ La_2(SO_4)_3,5K_2SO_4;$$
$$La_2(SO_4)_3,Na_2SO_4,2H_2O;$$
$$La_2(SO_4)_3,(NH_4)_2SO_4,2H_2O \text{ and } La_2(SO_4)_3,5(NH_4)_2SO_4.$$

It forms[2] double sulphates also with pyridine and quinoline sulphates.

Lanthanum Bromate,[3] $La(BrO_3)_3,18H_2O$, is a white crystalline compound, melting at 37·5° in its water of crystallisation. It is formed by the action of barium bromate on the sulphate, and dissolves to the extent of 416 parts in 100 of water at 25°.

Lanthanum Nitride, LaN, is a black powder which is formed by the direct union of its elements and is hydrolysed by water.

Lanthanum Nitrate, $La(NO_3)_3,6H_2O$, is easily soluble in water and alcohol, crystallising in oblique prisms or tablets. It forms double nitrates[4] with all the alkali metal nitrates and with ammonium nitrate of the formulæ:

$$3La(NO_3)_3,4NaNO_3,3H_2O;$$
$$La(NO_3)_3,2NaNO_3,H_2O;\ La(NO_3)_3,2KNO_3,H_2O;$$
$$3La(NO_3)_3,4KNO_3,4{\cdot}5H_2O;$$
$$3La(NO_3)_3,4RbNO_3,8H_2O;\ La(NO_3)_3,2RbNO_3,4H_2O;$$
$$3La(NO_3)_3,4Cs(NO_3),5H_2O;$$
$$La(NO_3)_3,2CsNO_3,H_2O \text{ and } La(NO_3)_3,2NH_4NO_3,4H_2O.$$

Double nitrates are formed also with thallium nitrate, pyridine nitrate, and quinoline nitrate.[5] A series of double nitrates[6] is formed with the nitrates of magnesium, nickel, cobalt, zinc, and manganese.

Lanthanum Carbide, LaC_2, is formed when a mixture of the oxide with sugar charcoal is heated in the electric furnace. It is a crystalline substance, and is readily attacked by acids. Water decomposes it with evolution of a mixture of acetylene, methane, a very small amount of ethylene, and traces of liquid and solid hydrocarbons.[7]

[1] Barre, *Compt. rend.*, 1910, **151**, 871.
[2] Kolb, Melzer, Merckle and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.
[3] James and Langelier, *J. Amer. Chem. Soc.*, 1909, **31**, 913.
[4] Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221; Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299.
[5] Kolb, Melzer, Merckle and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.
[6] Jantsch, *Zeit. anorg. Chem.*, 1912, **76**, 303.
[7] Moissan, *Compt. rend.*, 1896, **123**, 148.

Lanthanum Carbonate, $La_2(CO_3)_3.8H_2O$.—This occurs as lanthanite, a mineral which contains varying quantities of cerium, and crystallises in greyish-white, pink, or yellowish rhombic prisms. It occurs at Bastnäs in Sweden; also in Silurian limestone with the zinc ores of the Saucon Valley, Lehigh County, Pa., and in other localities in the United States. When a lanthanum salt is precipitated with a soluble carbonate this same salt is obtained in the form of glittering scales.

Lanthanum forms complex tungstates[1] with silver oxide, barium oxide, and ammonia.

Detection and Estimation of Lanthanum.

360 Lanthanum chloride yields a spectrum consisting of many very bright and characteristic lines, by means of which even traces of the metal can be readily detected. The salts of lanthanum possess an astringent sweet taste. They do not show an absorption spectrum, and, when quite pure, do not give a phosphorescence spectrum.

Lanthanum is determined quantitatively by precipitating it either as hydroxide or as oxalate, these being converted by ignition into the oxide. Lanthanum may be estimated volumetrically[2] by means of oxalic acid and potassium permanganate.

The atomic weight of lanthanum has been obtained at various times by many chemists, but with varying results. The most recent experiments, however, yield fairly concordant numbers. Thus Brauner and Pavlicek[3] found the atomic weight to be 139·04, and Jones[4] 138·77; the number at present (1913) adopted is 139·0.

CERIUM. Ce = 140·25.

361 The sources of this metal, which always occurs along with the rare earths, have already been mentioned, as well as the means by which it is separated (p. 777). The metal itself was first prepared by Mosander in the form of powder by heating the chloride with sodium. Wöhler afterwards

[1] Balke and Smith, *J. Amer. Chem. Soc.*, 1904, **25**, 1229.
[2] Druschel, *Amer. J. Sci.*, 1907, [iv], **24**, 197.
[3] *Journ. Chem. Soc.*, 1902, **81**, 1243.
[4] *Amer. Chem. J.*, 1902, **28**, 23; *Zeit. anorg. Chem.*, 1903, **36**, 92.

obtained it in the coherent state, and Hillebrand and Norton [1] have prepared it in large quantity by the electrolysis of the chloride, whilst Winkler prepared it by heating the dioxide with magnesium powder; it possesses the colour and lustre of iron, and is tolerably permanent in dry air, but in moist air tarnishes, becoming first of a yellow, then of a blue, and finally of a green colour. It is as soft and malleable as lead, and can be hammered and rolled, and, when warm, drawn into wire. The electrolytically prepared metal has a specific gravity of 6·628 (Hillebrand and Norton), 7·0424 (Muthmann and Weiss), 6·920 (Hirsch).[2] Cerium melts at 623° (Muthmann and Weiss). It takes fire more easily than magnesium, and when scratched with a wire or scraped with a knife the particles of finely-divided metal which are rubbed off take fire. The same phenomenon is observed when the metal is struck with a piece of flint, sparks of the metal flying off and burning with great brilliancy. The metal also burns in the flame with a much more brilliant light than magnesium. It reacts with the elements of the chlorine group, water, and acids in a similar way to lanthanum, but concentrated nitric acid converts it into a brown substance, which is probably chiefly cerium dioxide. The alloys of cerium with other metals are generally hard and brittle, but that with antimony is soft. The alloys with iron, nickel, tungsten, manganese, cadmium, and several other metals yield sparks when struck.[2] With tin [3] definite compounds of the formulæ Ce_2Sn, Ce_2Sn_3, and $CeSn_2$ have been isolated, and with aluminium [4] compounds of the formulæ Ce_3Al, Ce_2Al, $CeAl$, $CeAl_2$, and $CeAl_4$ are obtained. The salts of cerium find a limited application in medicine as a remedy for sickness.

According to Schützenberger [5] and Brauner [6] the cerium compounds prepared from cerite invariably contain small quantities of the derivatives of an element of lower atomic weight; this has, however, been disputed by other workers, and the question still requires investigation.[7]

[1] *Pogg. Ann.*, 1875, **155**, 631; 1875, **156**, 466; see also Muthmann, Hofer and Weiss, *Annalen*, 1902, **320**, 231; 1904, **331**, 1.

[2] *Trans. Amer. Electrochem. Soc.*, 1911, **20**, 57.

[3] Vogel, *Zeit. anorg. Chem.*, 1911, **72**, 319.

[4] *Ibid.*, 1912, **75**, 41.

[5] *Compt. rend.*, 1895, **120**, 663, 962. [6] *Chem. News*, 1895, **71**, 283.

[7] Boudouard, *Compt. rend.*, 1897, **125**, 772; Brauner, *Proc. Chem. Soc.*, 1898, **14**, 69; Wyrouboff and Verneuil, *Compt. rend.*, 1897, **125**, 1180; Drossbach, *Ber.*, 1900, **33**, 3506.

CERIUM COMPOUNDS.

Cerium and Oxygen.

362 Cerium forms three oxides: (1) a dioxide, CeO_2, (2) a sesquioxide, Ce_2O_3, and (3) a peroxide, CeO_3. The sesquioxide and the dioxide are basic, and yield corresponding series of salts known as the *cerous* and *ceric* salts, but the dioxide, like the corresponding lead compound, acts in many respects as a peroxide.

Cerous Hydroxide, $Ce(OH)_3$, is formed as a white precipitate when ammonia or potash is added to solutions of the cerous salts. On exposure to air it oxidises very rapidly, and becomes coloured reddish-violet. Cerium sesquioxide is not formed by heating the dioxide in a stream of hydrogen as was formerly stated, but in this way a dark-blue oxide is obtained which has a composition[1] approximating to Ce_4O_7. A hydroxide roughly corresponding to this last substance has also been obtained by allowing cerous hydroxide to oxidise partially in air.[2] According to Burger the dioxide is reduced by calcium to the sesquioxide. This is a yellowish-green powder, which absorbs oxygen when preserved, and burns in the air to form the dioxide.[3]

Cerium Dioxide, CeO_2, is formed when a cerium salt of a volatile oxy-acid is heated in the air, and is thus obtained as a white or pale straw-coloured powder, which assumes a reddish tinge on ignition. If obtained by the ignition of the hydrated oxide it has a salmon colour. It may be obtained in the crystalline form by igniting cerous chloride with borax in a wind furnace.[4] It dissolves in concentrated sulphuric acid, forming a dark yellow solution which has powerful oxidising properties, and evolves considerable quantities of active oxygen.

When the acid sulphate is heated with caustic potash, or when chlorine acts on cerous hydroxide suspended in water, the hydrated dioxide, $CeO_2,3H_2O$, is formed as a sulphur-yellow powder, whilst, if the hydroxide precipitated by the

[1] Meyer, *Zeit. anorg. Chem.*, 1903, **37**, 378; Sterba, *Ann. Chim. Phys.*, 1904, [8], **2**, 193.

[2] Wyrouboff and Verneuil, *Compt. rend.*, 1899, **128**, 501; see also *Ann. Chim. Phys.*, 1906, [8], **9**, 289.

[3] *Ber.*, 1907, **40**, 1652.

[4] Nordenskiöld, *Pogg. Ann.*, 1861, **114**, 612; see also Sterba, *Compt. rend.*, 1901, **133**, 294; *Ann. Chim. Phys.*, 1904, [8], **2**, 193.

action of ammonia on a solution of cerium sulphate is dried at 385°, a bright yellow hydroxide, $CeO_2,2H_2O$ or $Ce(OH)_4$, is obtained, which does not lose water to any considerable extent until heated to 600°.[1] The hydroxides dissolve in hydrochloric acid, yielding a deep yellow solution which on heating yields the trichloride, chlorine being simultaneously evolved. The dioxide behaves therefore both as a basic oxide and a peroxide. A higher hydrated *peroxide*, CeO_3,xH_2O, is also known.[2]

Cerium dioxide is used in the manufacture of mantles for incandescent gas burners. Mantles composed of thoria alone only give a dull light when heated in the Bunsen flame, whereas the addition of a small quantity of cerium oxide causes a brilliant incandescence. The maximum brilliancy is obtained when the mantles contain 99 per cent. of thoria and 1 per cent. of ceria, whilst a greater or a less amount of ceria causes a marked diminution in the intensity of the light. No fully satisfactory explanation of this phenomenon has as yet been given.

Cerous Compounds.

363 *Cerous Hydride*, CeH_3, is prepared by passing hydrogen over metallic cerium heated at 250–270°. It is a dark-blue or black powder, and takes fire spontaneously in air[3]; in moist air it decomposes very rapidly; it is decomposed also by acids with evolution of hydrogen[4] and formation of cerous salts.

Cerous Chloride, $CeCl_3$, is formed as a yellowish-white sublimate when the metal is heated in chlorine, or when an intimate mixture of the oxide and carbon is heated in this gas. It may also be prepared by heating the sulphide first in a stream of carbon dioxide and then in hydrogen chloride. Prepared in this way it is a white crystalline mass which dissolves in water with a hissing noise.[5] The boiling point of the solution in alcohol points to the formula $CeCl_3$. The hydrated salt, $2CeCl_3,15H_2O$, remains behind in ill-defined crystals when a solution of cerous oxide in hydrochloric acid is allowed to evaporate over sulphuric acid, and the hydrate, $CeCl_3,7H_2O$, has also been obtained in rhombic crystals. On

[1] Carnelley and Walker, *Journ. Chem. Soc.*, 1888, **53**, 84.

[2] de Boisbaudran, *Compt. rend.*, 1885, **100**, 605.

[3] Dafert and Miklauz, *Monatsh.*, 1912, **33**, 911.

[4] Muthmann and Kraft, *Annalen*, 1902, **325**, 261, 281; Kellinberger and Kraft, *ibid.*, 279.

[5] Muthmann and Stützel, *Ber.*, 1898, **31**, 1829; 1899, **32**, 3413.

heating, it decomposes with evolution of hydrogen chloride and formation of a basic chloride. When treated with hexamethylene tetramine [1] a compound is formed of the formula $CeCl_3,14H_2O,2C_6H_{12}N_4$. Cerous chloride is hydrolysed [2] to the extent of 0·14 per cent. in a 1/32 normal solution.

Cerous Bromide, $CeBr_3$, is obtained as a hygroscopic snow-white crystalline powder by passing hydrogen bromide over heated cerium sulphide.[3] The anhydrous bromide [4] may also be prepared by heating the oxide in a mixture of sulphur chloride and hydrobromic acid.

Cerous Iodide, $CeI_3,9H_2O$, forms transparent easily soluble crystals which readily decompose with evolution of iodine.

Cerous Sulphide, Ce_2S_3, is formed when the metal is burnt in the vapour of sulphur, when the oxide is heated in carbon disulphide vapour, and when cerous sulphate is heated in a current of sulphuretted hydrogen.[5] It is a brown or purple-black powder of specific gravity 5·1. When the oxide is fused with three parts of sodium pentasulphide, and the fused mass lixiviated with water, cerous sulphide is obtained in small crystals resembling Mosaic gold, which do not undergo alteration on exposure to the air.[6]

Cerous Sulphate, $Ce_2(SO_4)_3$, dissolves in water at 0° to the extent of 40 parts [7] in 100, whilst at 100°, 100 parts of water dissolve only 0·775. The solution yields a number of crystalline hydrates. With stannic sulphate [8] a double salt of the formula $CeHSn(SO_4)_4$ is formed as a microcrystalline powder. Crystalline derivatives are formed by cerous sulphate with pyridine [9] and quinoline sulphates.

Potassium Cerous Sulphate, $3K_2SO_4,Ce_2(SO_4)_3$, is formed when an equal or greater weight of potassium sulphate is added to a solution of cerous sulphate. It dissolves in about 56 parts of water at 20°, and is almost insoluble in a concentrated solu-

[1] Barbieri and Calzolari, *Atti. R. Accad. Lincei*, 1911, [v], **20**, i., 164.
[2] Denham, *Zeit. anorg. Chem.*, 1908, **57**, 378.
[3] Muthmann and Stützel, *Ber.*, 1899, **32**, 3413.
[4] Burion, *Compt. rend.*, 1907, **145**, 243.
[5] Muthmann and Stützel, *Ber.*, 1899, **32**, 3413; Sterba, *Ann. Chim. Phys.*, 1904, [8], **2**, 193.
[6] Compare Muthmann and Stützel, *Ber.*, 1899, **32**, 3413; Sterba, *Ann. Chim. Phys.*, 1904, [8], **2**, 193.
[7] Muthmann and Rölig, *Zeit. anorg. Chem.*, 1898, **16**, 450; compare Brauner, *Journ. Chem. Soc.*, 1888, **53**, 357.
[8] Weinland and Kühl, *Zeit. anorg. Chem.*, 1907, **54**, 244.
[9] Kolb, Melzer, Merckle and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.

tion of potassium sulphate. It dissolves readily, however, in acidified water, and on slow evaporation a double salt, $Ce_2(SO_4)_3,2K_2SO_4,3H_2O$, crystallises out. If less than the above proportion of potassium sulphate is added to a solution of cerous sulphate, another salt having the composition $Ce_2(SO_4)_3,K_2SO_4$ is formed as a granular crystalline mass.

Sodium and ammonium sulphates also form sparingly soluble double salts with cerium sulphate.[1]

Cerous Nitride, CeN, is readily prepared by heating cerium in a current of nitrogen. According to Dafert and Miklauz [2] pure cerium nitride cannot be got by the foregoing method; the pure substance is obtained by heating the hydride at 800°–900°, in a current of nitrogen. It is a lustrous yellow or bronze substance, stable in dry air, and is decomposed by water with formation of ammonia, hydrogen, and cerium dioxide.[3]

Cerous Nitrate, $Ce(NO_3)_3,6H_2O$, is a crystalline mass which begins to decompose about 200°. It is easily soluble in water and in alcohol, and forms crystalline double salts with ammonium,[4] sodium, potassium, rubidium,[5] cæsium, and thallium nitrates, and also with the nitrates of pyridine, quinoline, and piperidine.[6] A series of double nitrates [7] of the general formula $2Ce(NO_3)_3,3M(NO_3)_2,24H_2O$ is formed with magnesium, nickel, zinc, cobalt, and manganese.

Cerous Phosphate, $CePO_4$, occurs in the mineral monazite. This mineral often contains thorium, tin, manganese, and calcium in varying quantities. It crystallises in brownish hyacinth-red monoclinic crystals, and occurs in the Urals, in Norway, and in several localities in the United States and South America.

Cerous Carbonate, $Ce_2(CO_3)_3$, occurs in lanthanite, and may be obtained by precipitating a solution of cerous sulphate with ammonium carbonate. The precipitate thus obtained has the composition $Ce_2(CO_3)_3,5H_2O$, and on standing assumes the form of small silky needles.

[1] Wolff, *Zeit. anorg. Chem.*, 1905, **45**, 89; Barre, *Compt. rend.*, 1910, **151**, 871.

[2] *Monatsh.*, 1912, **33**, 911.

[3] Muthmann and Kraft, *Annalen*, 1902, **325**, 261.

[4] Wolff, *Zeit, anorg. Chem.*, 1905, **45**, 89.

[5] Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **30**, 299; Jantsch and Widgorow, *Zeit. anorg. Chem* , 1911, **69**, 221.

[6] Kolb, Melzer, Merckle and Teufel, *Zeit. anorg. Chem.*, 1908, **60**, 123.

[7] Jantsch, *Zeit. anorg. Chem.*, 1912, **76**, 303.

The nitrite,[1] bromate,[2] $Ce(BrO_3)_3,9H_2O$, perchlorate,[1] $Ce(ClO_4)_3\,9H_2O$, dithionate,[1] $Ce_2(S_2O_3)_3,12H_2O$, selenate,[3] $Ce_2(SO_4)_3,4H_2O$, ammoniomolybdate,[4] $(NH_4)_6Ce_2Mo_{14}O_{48},24H_2O$, silicotungstate,[5] $2(12WO_3)2SiO_2,3CeO,H_2O,27H_2O$, and complex ferrocyanide,[6] $NH_4CeFe(CN)_6$, have all been prepared.

Ceric Compounds.

364 *Ceric Fluoride*, CeF_4,H_2O, is obtained by acting on hydrated cerium dioxide with hydrofluoric acid, and on heating yields water and then hydrofluoric acid and free fluorine.[7] Ceric fluoride forms double compounds[8] with the fluorides of cadmium, copper, cobalt, nickel, and zinc which have the general formula $MF_2,2CeF_4,7H_2O$.

Ceric Sulphate, $Ce(SO_4)_2$.—When cerium dioxide is heated with concentrated sulphuric acid it is converted without dissolving into ceric sulphate.[9] The salt, after washing with acetic acid and drying in a vacuum over potash, is obtained as a yellow crystalline powder. It is very soluble in water, and the solution deposits a basic salt on warming. The hydrated salt, $Ce(SO_4)_2,4H_2O$, is obtained by dissolving the dioxide in dilute sulphuric acid and evaporating the salt in a vacuum over sulphuric acid. It is then deposited in the form of reniform masses consisting of fine crystals. In the moist state these are brown, whilst when dried they are yellow. When an excess of concentrated sulphuric acid is poured on the dioxide and the solution, diluted with water, gradually allowed to evaporate, *ceri-cerohydrosulphate* is deposited in fine red hexagonal crystals. Some doubt exists as to the exact composition of this compound, which is given by Brauner[10] as $2Ce(SO_4)_2,Ce_2(SO_4)_3,H_2SO_4,24H_2O$. On further evaporating the mother-liquor, yellow crystals of $Ce(SO_4)_2,4H_2O$ are deposited.

Ceric sulphate forms double sulphates with the sulphates of

[1] Morgan and Cahen, *Journ. Chem. Soc.*, 1907, **91**, 475.
[2] James and Langelier, *J. Amer. Chem. Soc.*, 1909, **31**, 913.
[3] Cingolani, *Atti R. Accad. Lincei*, 1908, [v], **17**, 254.
[4] Barbieri, *Atti R. Accad. Lincei*, 1908, [v], **17**, 540.
[5] Wyrouboff, *Bull. Soc. franç. Min.*, 1905, **28**, 201.
[6] Robinson, *Journ. Chem. Soc.*, 1909, **95**, 1358.
[7] Brauner, *Monatsh.*, 1882, **3**, 8.
[8] Rinbach and Kilian, *Annalen*, 1909, **368**, 101.
[9] Meyer and Aufrecht, *Ber.*, 1904, **37**, 140.
[10] *Zeit. anorg. Chem*, 1904, **39**, 261, where a summary of the literature is given; see also Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [8], **9**, 289.

the alkali metals, such as $Ce(SO_4)_2,2K_2SO_4,2H_2O$, a compound which is deposited in small yellow monoclinic crystals. Ceric sulphate is decomposed by water with formation of basic salts, the composition of which varies according to the quantity of water present.

Ceric Nitrate.—The normal salt is not known, but when a solution of the hydrated dioxide in nitric acid containing calcium nitrate is evaporated, long red crystals of a *basic nitrate*, $Ce(NO_3)_3OH,3H_2O$, are obtained.[1] If potassium nitrate be added to the acid solution, and the liquid allowed to crystallise in a vacuum over lime, yellow, glistening six-sided prisms are deposited, having the composition $2Ce(NO_3)_4, 2KNO_3,3H_2O$. Ceric nitrate also forms double salts with other nitrates.

Ceric Ammonium Nitrate,[2] $Ce(NO_3)_4,NH_4NO_3,2H_2O$, is prepared by the electrolytic oxidation of a mixture of cerous and ammonium nitrates.

Cerium Carbide, CeC_2, is obtained by heating cerium dioxide with sugar charcoal in the electric furnace, and forms a reddish-yellow transparent crystalline substance. On treatment with water it yields a mixture of 75 per cent. of acetylene, 4 per cent. of ethylene, and 21 per cent. of methane.[3]

Cerium Silicide, $CeSi_2$, is obtained when cerium dioxide is heated with silicon in the electric furnace.[4] It forms small crystals having a steely lustre and a specific gravity of 5·67.

Ceric Selenite,[5] $Ce(SeO_3)_2$, ceric dihydrogen arsenite,[5] $Ce(H_2AsO_4)_4,4H_2O$, ceric iodate,[6] and ceric monohydrogen arsenite,[5] $Ce(HAsO_4)_2,6H_2O$, have been prepared.

Detection and Estimation of Cerium.

365 The spark spectrum of cerium contains a number of bright lines, of which the brightest and most characteristic lie in the green and blue. A characteristic reaction for the cerium compounds is the precipitation of red ceric hydroxide when sodium hypochlorite is added to a colourless cerous salt; this

[1] Meyer and Jacoby, *Zeit. anorg. Chem.*, 1901, **27**, 359.

[2] Plancher and Barbieri, *Atti R. Accad. Lincei*, 1904, [v], **14**, i., 119.

[3] Moissan, *Compt. rend.*, 1896, **122**, 357; 1897, **124**, 1233; Muthmann, Hofer, and Weiss, *Annalen*, 1902, **320**, 231.

[4] Sterba, *Compt. rend.*, 1902, **135**, 170.

[5] Barbieri and Calzolari, *Ber.*, 1910, **43**, 2214.

[6] Barbieri, *Atti R. Accad. Lincei*, 1907, [v], **16**, i., 644.

dissolves in warm hydrochloric acid with evolution of chlorine. The other reactions have already been described.

In order to estimate cerium quantitatively the solution is precipitated with caustic potash, and the washed and dried precipitate is heated in the air in order to convert it into the dioxide, or it is precipitated as the oxalate and converted into the dioxide by heating. Cerium may be estimated volumetrically[1] by means of oxalic acid and potassium permanganate, and also by means of potassium ferricyanide and potassium permanganate.[2]

The Atomic Weight of cerium has been determined by several chemists. The early work of Bunsen[3] and Rammelsberg[4] gave low values; later, Brauner[5] and Robinson[6] found 140·2. Still more recently Brauner,[7] by the analysis of cerium oxalate and sulphate, obtained the number 140·25.

PRASEODYMIUM. Pr = 140·6.

366 The substance originally described as didymia by Mosander (p. 773) was found by Lecoq de Boisbaudran in 1879 to contain the oxide of another element, named by him samarium, from which it was separated by repeated fractional precipitation with ammonia. Didymia, freed from samaria, was then looked on as an individual substance until in 1885 Welsbach[8] succeeded in resolving it into the oxides of two distinct elements, which he termed praseodymium and neodymium. This was accomplished by the oft repeated fractional crystallisation, from a strong nitric acid solution, of the double nitrate of the metal with ammonium, or, in the last stage of the process, sodium nitrate. The separation can also be effected by means of the double magnesium nitrate (Drossbach), or the sulphate.[9]

These two substances have not up to the present been further resolved and appear to be true elements. They resemble one

[1] Meyer and Schweitzer, *Zeit. anorg. Chem.*, 1907, **54**, 104.

[2] Browning and Palmer, *Amer. J. Sci.*, 1908, [v], **26**, 83.

[3] *Annalen*, 1853, **86**, 265; 1858, **105**, 40. [4] *Pogg. Ann.*, 1859, **108**, 40.

[5] *Journ. Chem. Soc.*, 1885, **47**, 879; *Chem. News*, 1895, **71**, 283.

[6] *Proc. Roy. Soc.*, 1884, **37**, 150.

[7] Brauner and Batěk, *Zeit. anorg. Chem.*, 1903, **34**, 103; Brauner, *ibid.*, 207.

[8] *Monatsh.*, 1885, **6**, 477.

[9] Muthmann and Rölig, *Ber.*, 1898, **31**, 1718.

another closely in their chemical properties, but their salts differ very strikingly in colour, those of praseodymium being green, and those of neodymium rose-coloured. The proportions present in the old didymium are about 1 of praseodymium to 2 of neodymium.

Praseodymium has been prepared by Muthmann and Weiss by the electrolysis of the chloride. It has a yellowish colour and is unaffected by air, melts at 940°, and has the sp. gr. 6·4754.

Praseodymium and Oxygen.—This metal readily forms a *dioxide*, PrO_2, which is obtained pure[1] by heating the nitrate with potassium nitrate at 400–450°. It is a black powder which yields chlorine with hydrochloric acid, is reduced by hydrogen peroxide, and in acid solution oxidises cerous to ceric salts and manganous salts to permanganic acid. No stable salts derived from this oxide are known.

The *sesquioxide*, Pr_2O_3, is obtained by heating the dioxide or one of the intermediate oxides in hydrogen, and is a light green powder which readily dissolves in acids forming characteristic green salts. When this oxide or a salt of the metal with a volatile acid is heated, a dark coloured oxide is formed, the composition of which is intermediate between Pr_2O_3 and PrO_2 and varies with the conditions of formation. Various formulæ have been ascribed to this substance, such as Pr_4O_7, Pr_5O_9 and Pr_6O_{11}.

The *hydroxide*, $Pr(OH)_3$, is a light green amorphous powder. A hydrate of a peroxide, Pr_2O_5, is also known.

Praseodymium Chloride, $PrCl_3$, is a pale green crystalline mass, melting at 818°, density at 18° 4·017; it is very readily soluble in water and alcohol, and yields a hydrate with $7H_2O$.

The *fluoride*, PrF_3, is obtained[2] as a gelatinous precipitate when hydrofluoric acid is added to a solution of the nitrate; on warming it yields yellow glistening crystals.

The *bromate*, $Pr(BrO_3)_3,9H_2O$, is formed in the same way as cerous bromate.

Praseodymium Sulphate, $Pr_2(SO_4)_3$, crystallises with $8H_2O$ and forms green monoclinic crystals. Hydrates with 5, 12, and $15\frac{1}{2}H_2O$ are also known.

Praseodymium Nitrate, $Pr(NO_3)_3,6H_2O$, crystallises in long needles, and forms the double ammonium salt,

$$Pr(NO_3)_3,2NH_4NO_3,4H_2O.$$

[1] Brauner, *Proc. Chem. Soc.*, 1901, **17**, 66. [2] Popovici, *Ber.*, 1908, **41**, 634.

It also forms double nitrates with the nitrates of rubidium,[1] magnesium,[2] nickel, cobalt, zinc, and manganese.

The hydride, carbide, sulphides, and nitride resemble those of lanthanum in chemical properties.

Praseodymium is best detected by means of its absorption spectrum, which contains 5 bands, the maxima of which are situated at wave-lengths 596·8, 589·5, 481·2, 469·3, and 444·7 (Brauner). The oxide acts as an exciter of the phosphorescence of colourless oxides such as lanthana and yttria.

Praseodymium compounds colour the borax bead [3] yellowish-green in the oxidising flame and green in the reducing flame.

NEODYMIUM. Nd = 144·3.

367 Neodymium salts are very difficult to prepare free from samarium, but this was accomplished by Demarçay [4] in 1898.

Neodymium has a yellowish colour and slowly tarnishes in the air. It melts at 840°, and has the sp. gr. 6·9563.

Neodymium and Oxygen.—The only stable oxide is the *sesquioxide*, Nd_2O_3, which is a blue powder, and is not affected by ignition in the air. The *hydroxide* [5] is prepared by precipitating a solution of a neodymium salt with an alkali hydroxide. If the dried product is heated to 310° a greyish-brown substance, $2Nd_2O_3,3H_2O$, is formed whilst at 525°, Nd_2O_3,H_2O, a grey compound is formed. The unstable *dioxide*, NdO_2, is formed by the action of heat on the oxalate and nitrate in an atmosphere of oxygen.

The salts of neodymium are derived from the sesquioxide and are of a rose to a violet-red colour.[6] The *chloride* melts at 785°. It forms hydrates with $1H_2O$ and $6H_2O$, and derivatives with alcohol and pyridine. With gaseous ammonia the anhydrous chloride forms derivatives with 1, 2, 4, 5, 8, 11 and 12 molecules of ammonia. The bromide [7] is prepared in the same way as cerous bromide, and the fluoride [8] as praseodymium

[1] Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221.
[2] Jantsch, *Zeit. anorg. Chem.*, 1912, **76**, 303.
[3] Milbauer, *Zeit. anal. Chem.*, 1907, **46**, 457.
[4] *Compt. rend.*, 1898, **126**, 1039.
[5] Joye and Garnier, *Compt. rend.*, 1912, **154**, 510.
[6] See Matignon, *Ann. Chim. Phys.*, 1906, [8], **8**, 243; *Compt. rend.*, 1906, **142**, 276; Matignon and Trannoy, *ibid.*, 1042.
[7] Burion, *Compt. rend.*, 1907, **145**, 243. [8] Popovici, *Ber.*, 1908, **41**, 634.

fluoride. The *sulphate* is much less soluble than that of praseodymium, whilst the *double ammonium nitrate* is more soluble than the corresponding praseodymium salt. Double nitrates [1] corresponding with those of praseodymium are formed by neodymium nitrate.

The absorption spectrum contains more than 20 bands, one of which, of wave-length 469·1, almost coincides with one of the praseodymium bands. Neodymium salts impart a violet colour to the borax bead [2] when heated in the reducing flame, but no colour in the oxidising flame. Like praseodymia, the oxide excites phosphorescence in other colourless earths. The oxide when heated, especially in presence of other oxides, glows with light which yields a discontinuous spectrum, a phenomenon which was also observed with the old didymium oxide.

SAMARIUM. Sa = 150·4.

368 This element was discovered in samarskite by Lecoq de Boisbaudran in 1879, but its compounds were first obtained quite free from europium and gadolinium in 1904 by Urbain and Lacombe [3] by the fractional crystallisation of the double magnesium nitrates to which the corresponding bismuth salt had been added. In addition to the salts of the type SaX_3, samarium forms a subchloride, $SaCl_2$. It and europium are the only elements of the rare earth metals to form compounds of this type.

Metallic samarium is of a whitish-grey colour, melts at 1,300–1,400°, has a sp. gr. of about 7·7, and tarnishes in the air. The *oxide*, Sa_2O_3, has a faint yellow colour and does not form a higher oxide when heated in the air. The salts are topaz-yellow coloured and show a faint absorption spectrum, most of the bands being in the blue or violet. A large number of them have been described by Cleve.[4] The *chloride*, $SaCl_3$, is almost white, melts at 686°, and forms a hydrate with $6H_2O$, which crystallises in large yellow tablets. The anhydrous salt is soluble [5] in alcohol and pyridine, and with the latter substance forms a gelatinous substance on heating which redissolves on

[1] Jantsch and Widgorow, *Zeit. anorg. Chem.*, 1911, **69**, 221 ; 1912, **76**, 303.
[2] Milbauer, *Zeit. anal. Chem.*, 1907, **46**, 457.
[3] *Compt. rend.*, 1904, **138**, 1166.
[4] *Bull. Soc. chim.*, 1885, (2), **43**, 53.
[5] Matignon, *Ann. Chim. Phys.*, 1906, **8**, 402.

cooling. On heating in hydrogen it is reduced to samarous chloride, and on heating in oxygen it yields an oxychloride, SaOCl. When treated with ammonia,[1] derivatives containing 1, 2, 3, 4, 5, 8, 9·5, and 11·5 molecules of ammonia are formed. The *subchloride*, $SaCl_2$, is formed when the chloride is heated in dry hydrogen or ammonia, or with aluminium powder.[2] It is a reddish-brown crystalline mass which dissolves in water, forming a red-brown solution which decomposes with evolution of hydrogen and becomes colourless. A corresponding subiodide, SaI_2, has also been prepared.

EUROPIUM. Eu = 152·0.

369 The salts of this element were first obtained from Lecoq de Boisbaudran's samarium by Demarçay (1896), and were first prepared pure by Urbain and Lacombe (1904). The separation from samarium is effected by the prolonged fractional crystallisation from nitric acid of the magnesium double nitrates in presence of bismuth nitrate, the double magnesium nitrate of which is intermediate in solubility between the other two. The oxide, Eu_2O_3, and the salts have a faint pink colour, and the latter show a faint absorption spectrum. This element, like samarium, forms a lower chloride,[3] $EuCl_2$, by heating the higher chloride in hydrogen. The spark spectrum is brilliant and characteristic. Europium occurs in very small quantities, monazite sand containing only 0·02 per cent. Its presence has been detected in the sun and certain stars.[4]

GADOLINIUM. Gd = 157·3.

370 This element was discovered in 1880 by Marignac[5] in samarskite, and its salts were first prepared free from europium and terbium by Urbain and Lacombe.[6] The oxide, Gd_2O_3, is white and the salts are colourless and do not show absorption bands.[7]

[1] Matignon and Trannoy, *Compt. rend.*, 1905, **140**, 141.
[2] Matignon and Cazes, *Ann. Chim. Phys.*, 1906, [8], **8**, 417.
[3] Urbain and Bourion, *Compt. rend.*, 1911, **153**, 1155.
[4] Lunt, *Proc. Roy. Soc.*, 1907, **79**, A, 118.
[5] *Ann. Chim. Phys.*, 1880, [5], **20**, 535.
[6] See also Urbain, *Compt. rend.*, 1905, **140**, 583.
[7] Benedicks, *Zeit. anorg. Chem.*, 1900, **22**, 393; Popovici, *Ber.*, 1908, **41**, 634.

TERBIUM. Tb = 159·2.

371 The existence of the earth originally called erbia by Mosander was denied by Berlin (1860), and by Bahr and Bunsen (1866), but was confirmed by Delafontaine (1878) and by Marignac. It then received the name of terbia, the designation erbia having been in the meanwhile applied to the rose-red earth described below. It was afterwards found that all these preparations consisted mainly of gadolinium, and pure terbium compounds were first obtained by Urbain [1] by fractionating the nickel double nitrates, the ethyl sulphates, or a mixture of bismuth nitrate with the nitrates of the terbium earths. According to Urbain, terbium forms a white oxide, Tb_2O_3, and a dark brown peroxide, which appears to have the composition Tb_4O_7, and is obtained by igniting the oxalate. The sesquioxide is strongly magnetic.[2] The salts [3] are colourless and show no absorption spectrum. The presence of terbia in gadolinia renders the latter yellow.

DYSPROSIUM. Dy = 162·5.
HOLMIUM. Ho = 163·5.
ERBIUM. Er = 167·7.
THULIUM. Tm = 168·5.

372 The terbia originally isolated from crude yttria by Mosander subsequently received the name of *erbia* (Berlin), and has been shown by Soret, Cleve, Thalén and Lecoq de Boisbaudran to consist of at least four earths, the true *erbia*, *holmia*, *thulia*, and *dysprosia*. The salts of all these show absorption bands, but it is doubtful whether any one of the four, with the possible exception of dysprosia,[4] is an individual substance.[5] Thulium, according to Auer von Welsbach,[6] consists of at least three elements, which he names thulium I, II, and III respectively.

[1] *Compt. rend.*, 1905, **141**, 521; 1906, **142**, 957; *J. Chim. phys.*, 1906, **4**, 31, 105.

[2] Urbain and Jantsch, *Compt. rend.*, 1908, **147**, 1286.

[3] Potratz, *Chem. News*, 1905, **92**, 3; Urbain and Jantsch, *Compt. rend.*, 1908, **146**, 127.

[4] Urbain, *Compt. rend.*, 1906, **142**, 785; **143**, 592.

[5] Compare *Zeit. anorg. Chem.*, 1892, **3**, 353, 407.

[6] *Monatsh.*, 1911, **32**, 373.

Erbium forms a rose-coloured oxide and salts of the same colour, which in solution show absorption bands, whilst the salts[1] of dysprosium are green or yellow. Dysprosium oxide is very strongly magnetic,[2] being 12·8 times as strong as ferric oxide. Holmia is yellow in colour[3] and the salts are pale yellow.

NEO-YTTERBIUM. Yb = 172·0.
LUTECIUM. Lu = 174·0.

373 The element known as ytterbium was discovered by Marignac in gadolinite in 1878,[4] and was separated from scandium by Nilson in 1880. It forms one oxide of the type M_2O_3, which is white; the salts are colourless and yield no absorption bands, but the spark spectrum is characteristic (Thalén). Urbain,[5] by fractional crystallisation of the nitrate of pure ytterbia, has resolved it into two elements which he terms lutecium and neo-ytterbium; of the three characteristic absorption bands of the "old" ytterbium the α and β bands belong to neo-ytterbium and the γ band to lutecium. The atomic weights[6] were determined by analysis of the hydrated sulphates prepared from the nitrates which had been subjected to 15,000 recrystallisations. Auer von Welsbach,[7] by the fractional precipitation of ytterbium oxalate, has also resolved ytterbium into two components which he terms *aldebaranium* and *cassiopeium*, these elements are identical with neo-ytterbium and lutecium. Welsbach is of the opinion that a third element also is present, since some of the lines present in the spectrum of the old ytterbium do not appear in the spectra of either of the new elements. The compounds of the two elements are indistinguishable chemically, and have been investigated by Urbain, Bourion, and Maillard.[8]

CELTIUM. Ct.

In the isolation of lutecium from the gadolinite earths Urbain[9] obtained a small quantity of an uncrystallisable

[1] Jantsch and Ohl, *Ber.*, 1911, **44**, 1274.
[2] Urbain, *Compt. rend.*, 1908, **146**, 922.
[3] Holmberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, No. 2, 1.
[4] *Compt. rend.*, 1878, **87**, 578.
[5] Urbain, *Compt. rend.*, 1907, **145**, 759.
[6] *Compt. rend.*, 1908, **146**, 408.
[7] *Monatsh.*, 1908, **29**, 181.
[8] *Compt. rend.*, 1909, **149**, 127.
[9] *Compt. rend.*, 1911, **152**, 141.

mother-liquor, which contained an element whose oxide had a magnetic susceptibility 3–4 times less than that of lutecia. The name *celtium* was assigned to the element. The arc spectrum of this oxide is rich in lines, the most intense being $\lambda = 2685{\cdot}2$, $2765{\cdot}8$, $3080{\cdot}7$, $3118{\cdot}6$, and $3197{\cdot}9$. The oxide is less basic than lutecia but more basic than scandia.

GROUP IV.

Sub-group (*a*)	*Sub-group* (*b*)
Carbon.	Silicon.
Titanium.	Germanium.
Zirconium.	Tin.
(Cerium).	Lead.
Thorium.	

374 In this group there is no well-defined division of the elements composing it into two distinct sub-groups, such as is noticeable in the others of the first seven groups, and the differences observable between the members of the odd and even series are only of minor importance.

Cerium probably belongs to this group, but as its chemistry is so intimately connected with that of the other members of the group of rare earth metals it has been described along with them (p. 788).

The first two members of this group, carbon and silicon, have already been described among the non-metallic elements. Both exist in the amorphous and crystalline states, silicon melting only at a very high temperature, whilst carbon has not yet been melted, although it volatilises at the highest attainable temperatures. The remaining elements have all metallic properties, and, with the exception of tin and lead, possess high melting points; in the compact state they undergo at most a surface oxidation in the air at the ordinary temperature, but when strongly heated readily combine with oxygen, and, except in the case of lead, the oxide formed in presence of an excess of oxygen is the *dioxide*. The dioxides of the members having the lower atomic weights, including those of carbon and silicon, behave chiefly as acid-forming oxides, but they become more basic as the atomic weight of the element increases. These oxides correspond in each case with a series of salts in which

the element is tetravalent, and, except in the case of lead, this series includes the most important compounds. Lead in its most characteristic compounds is divalent, and, as is so frequently the case with elements having a high atomic weight, it presents many resemblances to the elements having the next lowest and next highest atomic weights, viz., thallium and bismuth.

A very characteristic series of double salts with the alkali halides is yielded by the tetrahalogen derivatives of most of these elements, the double fluorides, which have the general formula $M^{I}_{2}M^{IV}F_{6}$, being the most important. In the case of silicon, titanium, germanium, zirconium, and tin, these compounds are isomorphous, but this appears not to be the case with the thorium compound. The corresponding salt of lead has not been prepared, but an acid salt, PbF_4,3KF,HF, exists, which is isomorphous with the analogous tin salt, SnF_4,3KF,HF.

Carbon is distinguished from all other elements by the property possessed by its atoms of uniting together in open or closed chains, forming nuclei, which may contain as many as sixty atoms, and which, in combination with the other elements, give rise to the immense number of carbon compounds. The same property is observable to a very small extent in silicon, but not in the other members of the group. In addition to the typical elements, carbon and silicon, only germanium, tin, and lead, *i.e.*, the members of the "odd" series, yield organometallic derivatives.

THE TITANIUM GROUP.

TITANIUM. Ti=48·1.

375 The Rev. William Gregor[1] in 1789 discovered a new metal contained in the mineral menachanite or ilmenite, occurring in Cornwall. In 1795 Klaproth investigated the composition of the mineral rutile, and discovered in it a new metal to which he gave the name of titanium. In a subsequent investigation of ilmenite, in 1797, he found that the metal which that mineral contained was titanium. Klaproth found that rutile consisted mainly of titanium dioxide, but he did not succeed in obtaining

[1] *Crell. Ann.*, 1791.

the oxide in the pure state, this having been first accomplished by Rose in 1821.

Titanium is a comparatively rare element, and is not found in the metallic state. It occurs as the dioxide, TiO_2, in three minerals, rutile, brookite, and anatase, which possess different crystalline forms, and also in combination with ferrous and ferric oxides in titanic iron ore or ilmenite, $FeTiO_3$; and with lime and oxide of iron in perofskite, $(Ca,Fe)TiO_3$, as well as in titanite or sphene, $CaTiSiO_5$; schorlomite, $Ca(Ti,Fe)SiO_5$, and keilhauite, $CaYt(Ti,Al,Fe)SiO_5$. Magnetic iron ore also frequently contains larger or smaller quantities of titanium dioxide, and this titanium finds its way into many blast-furnace slags and pig-irons. Titanium occurs in small quantity in several other minerals, and traces have been found in trap and basalt, in many amphiboles and micas, and in garnet; hence it occurs in most fertile soils, in many clays, and likewise in certain mineral waters. It has been found in human and ox flesh and bone,[1] and occurs in the ashes of all plants[2] and in many peats,[3] whilst its presence has been detected in certain meteorites, and it forms an important constituent of the solar atmosphere.

Preparation of Metallic Titanium.—It appears very doubtful whether metallic titanium has yet been obtained in the pure condition; the usual methods for the reduction of the oxide, such as heating with metallic sodium and magnesium, yield products which still contain considerable quantities of titanium monoxide, and the product obtained by the action of sodium on halogen derivatives of titanium also usually contains small quantities of the monoxide, formed by the action of the moisture present, and of the nitride, obtained by the direct union of the metal with nitrogen, which it is almost impossible completely to exclude. Owing to the extreme readiness with which titanium and nitrogen combine at high temperatures, and to the metallic appearance of the nitride, this compound was mistaken by the earlier investigators for the metal itself, as was also the compound which it forms with carbon and nitrogen, now known as titanium cyanonitride.

The nearest approach to the pure element has been obtained by Moissan, who fused carbon with an excess of titanium dioxide

[1] Baskerville, *J. Amer. Chem. Soc.*, 1899, **21**, 1099.
[2] Wait, *J. Amer. Chem. Soc.*, 1896, **18**, 402; Lippmann, *Ber.*, 1897, **30**, 3037.
[3] Baskerville, *J. Amer. Chem. Soc.*, 1899, **21**, 402.

at a very high temperature in the electric furnace. Three distinct layers are found in the solidified product, the uppermost consisting of titanium containing about 5 per cent. of carbon, the second of the nitride, and the third of titanium monoxide. If the top layer be heated again with an excess of titanium dioxide the quantity of carbon is reduced to 2 per cent., and the product is free from nitrogen and silicon.[1] Thus prepared titanium has a brilliant white fracture and is hard enough to scratch rock crystal and steel, but is extremely friable. It has a specific gravity of 4·87, and on heating combines with the halogens and oxygen with incandescence, It dissolves in cold dilute sulphuric acid with evolution of hydrogen, and also in hot concentrated hydrochloric acid, aqua regia, and more slowly in nitric acid, and decomposes steam at 700–800°. Moissan [2] has distilled this titanium in the electric furnace by the use of a current of great intensity, the metal condensing in small crystals.

Nilson and Pettersson[3] prepared metallic titanium by enclosing the requisite quantities of titanium tetrachloride and sodium in an air-tight cylinder of mild steel, and exposing the latter to a red heat. The metal is thus obtained in yellow scales, which have frequently a bluish surface colour. These, however, still contain a considerable quantity of oxygen, probably as the monoxide. A still less pure product is obtained by heating potassium titanofluoride with sodium; the amorphous powder thus obtained resembles reduced iron in appearance and contains oxygen and usually nitrogen in addition. A very much purer product has been obtained by heating titanium oxide in an evacuated iron vessel with calcium shavings.[4]

Titanium combines with nitrogen with extreme readiness, in this respect resembling boron and magnesium; the reaction commences at about 800°, and the nitride is also formed together with the oxide when the metal burns in the air.

Metallic titanium in the form of its alloys is used in the steel industry. It appears to exert a refining effect. The tensile strength of the steel is improved. Steel to which a small quantity of titanium has been added is largely used on the American railways and for bridge construction.

[1] Moissan, *Compt. rend.*, 1895, **120**, 290.
[2] *Compt. rend.*, 1906, **142**, 673.
[3] *Zeit. physikal. Chem.*, 1887, **1**, 25.
[4] Wedekind, *Annalen*, 1913, **395**, 149.

TITANIUM COMPOUNDS.

Titanium and Oxygen.

376 Titanium combines with oxygen to form a number of oxides, the most important being:

Titanium dioxide, TiO_2.
Titanium sesquioxide, Ti_2O_3.
Titanium peroxide, TiO_3.

In addition to these the monoxide, TiO, has been prepared, and oxides of the formulæ Ti_3O_4, Ti_3O_5, and Ti_7O_{12} have been described; the existence of the last three is, however, doubtful.

Titanium Monoxide, TiO, is obtained in the form of black prismatic crystals by heating the dioxide strongly in the electric furnace,[1] and is also formed, together with magnesium titanate, when titanium dioxide is heated with the requisite quantity of magnesium powder:[2]

$$2TiO_2 + Mg = TiO + MgTiO_3.$$

Titanium Sesquioxide, Ti_2O_3, is obtained by strongly igniting titanium dioxide in a current of hydrogen and allowing the product to cool in the gas. The same oxide may also be obtained as a copper-coloured, lustrous crystalline mass, together with the trichloride and oxychloride of titanium, by passing a mixture of hydrogen and the vapour of titanium tetrachloride over white-hot titanium dioxide. It is not attacked by nitric or hydrochloric acid, but sulphuric acid dissolves it with formation of a violet solution (Ebelmen).

The *hydrated sesquioxide* is formed by digesting a solution of titanic acid in hydrochloric acid with metallic copper at 20°–40°; the solution attains a violet-blue colour, and when poured into aqueous ammonia yields a dark-brown precipitate of titanous hydroxide (Fuchs). The hydroxide is formed also when a solution of the trichloride is precipitated by alkalis.

When titanium sesquioxide is shaken with milk of lime in the presence of oxygen it is oxidised to the dioxide. More oxygen is absorbed than is necessary for this change, whilst hydrogen peroxide is formed in amount corresponding to the whole of the oxygen absorbed. Water must therefore take

[1] Moissan, *Compt. rend.*, 1892, **115**, 1034.
[2] Winkler, *Ber.*, 1890, **23**, 2658.

part in the reaction, and the phenomenon is probably a case of autoxidation (see Vol. I., p. 253). In the same way, when the sesquioxide is oxidised by a solution of chromic acid in the presence of potassium iodide, or by potassium permanganate in the presence of tartaric acid, titanic acid is formed, and at the same time oxidation of the potassium iodide or tartaric acid is brought about.[1]

Titanium Dioxide, TiO_2, is trimorphous, occurring as three different minerals. rutile, anatase, and brookite. Rutile crystallises in tetragonal prisms, having a specific gravity of 4·18–4·25, isomorphous with those of tin dioxide or cassiterite, and possessing an adamantine lustre and a brown or reddish colour. Anatase crystallises in a totally different form of the tetragonal system, has a specific gravity of 3·82–3·95, and a brown or black colour. Brookite crystallises in flat rhombic prisms and has a specific gravity of 3·86–4·23.

Amorphous titanium dioxide is obtained by the decomposition of aqueous titanium chloride by ammonia, the precipitate being washed, dried, and ignited; or it may be directly prepared from rutile or titanic iron ore. In order to prepare the pure oxide from rutile, the finely-powdered mineral is fused with three times its weight of potassium carbonate, the solidified mass powdered and dissolved, in a platinum vessel, in dilute hydrofluoric acid, potassium titanofluoride being thus formed and the ferric oxide left free from titanium. The mass is then heated with sufficient water to dissolve the whole of the titanium double salt, the liquid boiled and filtered hot. On cooling, the mass of the titanofluoride crystallises out, and this, after washing with cold water, may be purified by recrystallisation. The titanofluoride is then dissolved in hot water and the titanium precipitated by ammonia as titanic hydroxide containing ammonia, which on ignition yields pure titanium dioxide (Wöhler). Pure titanic oxide may also be obtained from titanic iron ore in a similar manner, or by fusing it with potassium bisulphate, or by igniting it in a mixture of chlorine and hydrochloric acid when ferric chloride is volatilised (Friedel and Guérin):

$$2FeTiO_3 + 4HCl + Cl_2 = 2FeCl_3 + 2TiO_2 + 2H_2O.$$

Amorphous titanium dioxide is a white, tasteless powder which when gently heated has a lemon-yellow colour, and when

[1] Manchot and Richter, *Ber.*, 1906, **39**, 320, 488.

strongly ignited appears brown. It has a specific gravity of from 3·89 to 3·95, and when very strongly heated this rises to 4·25.

When it is heated with microcosmic salt (Ebelmen) or with borax (G. Rose) for some time to a white heat, fine crystals of rutile are obtained, which have a specific gravity of 4·26. Crystalline titanium dioxide can also be obtained by passing the gases obtained by decomposing molten potassium titanofluoride with hydrogen chloride through a hot platinum tube into which a current of moist air and hydrogen is also passed. In this way Hautefeuille[1] has shown that by treatment at a temperature not exceeding the boiling point of cadmium (778°), anatase is produced, the crystals of which have a specific gravity of 3·7 to 3·9; at a temperature of about 1,000°, steel-blue coloured rhombic crystals of brookite are obtained, which have a specific gravity of 4·1, and closely resemble the natural crystals from Miask. At still higher temperatures again, rutile is produced, so that this last is the only form which is stable at a high temperature, and in an acid or moist atmosphere.[2]

At the temperature of the oxy-hydrogen flame titanium dioxide fuses, forming a thin liquid, which solidifies to a confused crystalline mass.

In its chemical properties titanium dioxide closely resembles the corresponding silicon dioxide, behaving as an acid anhydride. It is insoluble in water, hydrochloric acid, and dilute sulphuric acid, although it dissolves when digested for some time with hot concentrated sulphuric acid. The amorphous oxide dissolves on fusion with alkalis or alkali carbonates, unless it has been strongly ignited, forming the titanates, and also dissolves slowly in fused potassium hydrogen sulphate, yielding a clear mass which dissolves perfectly in warm water. When this solution is boiled, the hydrated dioxide is precipitated. Titanium dioxide corresponds to the most important series of titanium salts in which the metal is tetravalent.

Titanic Acid and the Titanates.—As is the case with the analogous silicic acid, several hydrates of varying composition are known. There appears to be little doubt that the hydrates *orthotitanic acid*, $Ti(OH)_4$, and *metatitanic acid*, $TiO(OH)_2$, exist, but in addition others have been prepared containing quantities of water intermediate between the amounts

[1] *Ann. Chim. Phys.*, 1865, [4], **4**, 129.

[2] Friedel and Guérin, *Bull. Soc. chim.*, 1874, **22**, 482.

required for these two formulæ, and also with less than that required by the latter formula. These may possibly be the hydrates corresponding to the complex titanic acids, but they have not been obtained of sufficiently definite composition to enable this to be ascertained.

Orthotitanic Acid, $Ti(OH)_4$, is obtained by adding an alkali to a cold hydrochloric acid solution of a titanate, and forms a voluminous white precipitate which is soluble in dilute hydrochloric acid and sulphuric acid, and loses water on drying, forming other hydrates. When heated it is converted into the anhydride, the reaction being accompanied by evolution of light. When allowed to remain under water it is gradually converted into metatitanic acid.[1]

Metatitanic Acid, $TiO(OH)_2$, is obtained by boiling a solution of orthotitanic acid in hydrochloric acid, or by the action of nitric acid of specific gravity 1·25 on titanium. It is insoluble in acids with the exception of concentrated sulphuric acid. When heated it is converted into the anhydride without evolution of light.

The other hydrates also are frequently spoken of as "ortho" or "meta" acids, according as they are soluble or insoluble in dilute acids.

By the dialysis of a hydrochloric acid solution of orthotitanic acid, Graham obtained a solution of colloidal titanic acid, and von der Pfordten has also obtained the acid as a colourless jelly.[2]

Potassium Titanate, K_2TiO_3, is formed as a yellow, fibrous mass when the dioxide is fused with potassium carbonate. On boiling titanic acid with caustic potash and evaporating the solution, colourless, readily soluble prisms of $K_2TiO_3,4H_2O$ are deposited. When a hydrochloric acid solution of titanic acid is precipitated with potassium carbonate, an amorphous precipitate of potassium trititanate, $K_2Ti_3O_7,2H_2O$, is thrown down, and this in presence of hydrochloric acid is converted into a hexatitanate, $K_2Ti_6O_{13},2H_2O$. The fused anhydrous normal salt, when treated with water in excess, also yields a trititanate, $K_2Ti_3O_7,3H_2O$, as a fine crystalline powder.

Calcium Titanate, $CaTiO_3$.—This occurs in the Urals, in the valley of Zermatt in Switzerland, and at Magnet Cove, Arkansas, as the mineral perofskite, which contains in addition 1 to 6 per cent. of ferrous oxide, as well as traces of manganese and magnesium. It forms rhombic crystals having a metallic or ada-

[1] Wagner, *Ber.*, 1888, **21**, 960. [2] *Annalen*, 1887, **237**, 213.

mantine lustre, a yellow or iron-black colour, and a specific gravity of 4·0. The crystals can be artificially obtained by strongly igniting a mixture of titanium dioxide, lime, and calcium carbonate (Ebelmen).

Calcium Titanosilicate, $CaTiSiO_5$, is found as titanite or sphene in brown, green, or black monoclinic crystals, having an adamantine or resinous lustre and a specific gravity of 3·4 to 3·56, occurring imbedded in granite, gneiss, mica-schist, and granular limestone. Titanite can be obtained artificially by fusing calcium chloride with titanium dioxide and silica. The mineral guarinite has the same composition as titanite, and is found in tetragonal crystals, having a specific gravity of 3·487, in small cavities in a greyish trachyte at Monte Somma.

Ilmenite, or *Titanic Iron Ore*, $FeTiO_3$.—This mineral, the one in which titanium was first discovered, occurs tolerably widely distributed, and crystallises in black hexagonal crystals. One of its most important localities is Krageroe, in Norway. Fine crystals are also found in Warwick Co., New York, and vast deposits occur at Bay St. Paul, in Canada. It is frequently found in the finely-divided state as sand on the shores of the Mersey opposite Liverpool, in New Zealand, and elsewhere. Its specific gravity ranges from 4·5 to 5, and its composition is a variable one. It was thought to be an isomorphous mixture of the sesquioxides of titanium and iron, but is now regarded as a derivative of titanium dioxide. Many ilmenites contain magnesia,[1] and the formula has sometimes been written as $(Fe,Mg)O,TiO_2$.

Titanium Trioxide, or *Titanium Peroxide*, TiO_3, is obtained by dropping titanium chloride into dilute alcohol and adding a large excess of hydrogen peroxide to the solution. Ammonia, ammonium carbonate, or potash is then added, and after a time a bright yellow precipitate separates out. The precipitate consists of a hydrate of titanium trioxide, which retains water and salts very persistently, and dissolves in hydrochloric acid with evolution of a little chlorine and formation of a yellowish-red solution.[2]

When titanium trioxide is treated at 0° with hydrogen peroxide, and potash and alcohol are then added, crystals of *potassium peroxide hypertitanate*, $K_2O_4,TiO_3,K_2O_2,10H_2O$, separate out, whilst if soda is used in place of potash the compound

[1] Penfield and Foote, *Amer. J. Sci.*, 1897, [4], **4**, 108.

[2] Classen, *Ber.*, 1888, **21**, 370.

formed has the composition $(Na_2O_2)_4,Ti_2O_7,10H_2O$. These substances are stable at 0°, but lose oxygen at ordinary temperatures.[1]

Titanium and the Halogens.

377 *Titanium Trifluoride,* TiF_3, is obtained as a violet powder by igniting potassium titanofluoride in a current of hydrogen and treating the product with hot water. It combines with ammonium fluoride, forming several double salts.

Titanium Tetrafluoride, TiF_4, is obtained by the action of fluorine on warm, finely-powdered titanium, or of anhydrous hydrofluoric acid on titanium tetrachloride at 100°–120°, or on powdered titanium at a red heat,[2] and also by the action of liquid anhydrous hydrofluoric acid on the tetrachloride.[3] It may also be prepared by heating barium titanofluoride to a red heat.[4] It is a white solid at the ordinary temperature, boils at 284°, and has the specific gravity 2·798 at 20·5°, whilst its vapour density at 444° corresponds with the formula TiF_4. It is very hygroscopic and dissolves in water to a clear solution, which on evaporation deposits crystals of $TiF_4,2H_2O$. With dry ammonia it forms the compound $TiF_4,2NH_3$, which sublimes without decomposition and is soluble in water. Titanium tetrafluoride is decomposed by hot sulphuric acid with formation of the dioxide.

When titanium dioxide is dissolved in hydrofluoric acid a syrupy liquid is obtained, which probably contains *hydrogen titanofluoride,* H_2TiF_6. The *titanofluorides* are isomorphous with the silicofluorides, zirconofluorides, and stannifluorides.

Potassium Titanofluoride or *Potassium Fluotitanate,* K_2TiF_6.—This salt may be prepared by the action of potassium hydrogen fluoride on a solution of titanium dioxide in excess of concentrated hydrofluoric acid. It crystallises in small lustrous leaflets, which may be recrystallised without change from hydrofluoric acid.[5] The hydrated salt, K_2TiF_6,H_2O, is prepared either by adding potash to aqueous hydrogen titanofluoride (Berzelius), or, according to Wöhler, by fusing titanium dioxide in a platinum crucible with twice its weight of potassium carbonate and

[1] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 678.
[2] Ruff and Ipsen, *Ber.*, 1903, **36**, 1777.
[3] Ruff and Plato, *Ber.*, 1904, **37**, 673.
[4] Emich, *Monatsh.*, 1904, **25**, 1907.
[5] Marchetti, *Zeit. anorg. Chem.*, 1895, **10**, 66.

dissolving the fused and pulverised mass in a platinum dish in the requisite quantity of dilute hydrofluoric acid. The potassium salt then crystallises out in shining scales closely resembling those of boric acid and belonging to the monoclinic system (Marignac); they may be dried between filter paper and recrystallised from boiling water. It loses its water at 100°, and melts without decomposition at a white heat. The anhydrous salt may be obtained from the hydrated salt by recrystallisation from concentrated hydrofluoric acid (Marchetti). When a warm solution of potassium titanofluoride is treated with hydrogen peroxide, *potassium titanoperoxyfluoride*, $TiO_2F_2,2KF$, is formed.[1]

Sodium Titanofluoride, Na_2TiF_6, is obtained in a similar manner to the preceding salt in hexagonal prisms most probably isomorphous with sodium silicofluoride (Marignac). A solution containing an excess of hydrofluoric acid deposits small glistening rhombic crystals having the composition $Na_2TiF_6,NaHF_2$.

Ammonium Titanofluoride, $(NH_4)_2TiF_6$.—This salt was obtained by Berzelius, in rhombohedra isomorphous with the corresponding tin compound, by neutralising hydrogen titanofluoride with ammonia. A second ammonium salt having the composition $(NH_4)_2TiF_6,NH_4F$ separates in tetragonal crystals from a solution of the preceding salt in an excess of ammonium fluoride.

Titanium Dichloride, $TiCl_2$, was obtained by Friedel and Guerin [2] by passing dry hydrogen at a dull red heat over titanium trichloride. This compound is a very hygroscopic light-brown powder, which can be volatilised in hydrogen at a red heat without fusion. It burns like tinder on exposure to air, giving off fumes of titanium tetrachloride and leaving a residue of titanium dioxide. It hisses when thrown into water, evolving hydrogen and yielding a yellow liquid.

Titanium Trichloride, $TiCl_3$.—When the vapour of titanium tetrachloride mixed with hydrogen is passed through a red-hot tube, dark violet scales of the trichloride are deposited (Ebelmen). It may also be obtained by heating titanium tetrachloride in a closed tube with molecular silver at 180–200°:

$$TiCl_4 + Ag = TiCl_3 + AgCl.$$

If the mixture thus obtained is heated more strongly, the

[1] Piccini, *Zeit. anorg. Chem.*, 1895, **10**, 438.
[2] *Ann. Chim. Phys.*, 1876, [5], **7**, 24.

reverse action takes place (Friedel and Guérin). Titanium trichloride has also been obtained by the electrolytic reduction of a solution of titanium tetrachloride in dilute hydrochloric acid, violet crystals of the composition $TiCl_3,6H_2O$ being deposited when the resulting liquid is either evaporated in vacuo or saturated at 0° with dry hydrochloric acid.[1]

Titanium trichloride is non-volatile, and on heating decomposes into the dichloride and tetrachloride. When heated in the air, thick vapours of titanium tetrachloride are emitted and titanium dioxide is left behind. It readily deliquesces on exposure to moist air and dissolves in water with evolution of heat, yielding a reddish-violet solution.

Titanium trichloride is a powerful reducing agent. Thus when boiled with aqueous sulphurous acid, sulphur separates out, whilst nitric acid and the nitrates are reduced by it to ammonia (Knecht), and the salts of gold, silver, and mercury to the metals. Standard solutions of titanium trichloride have been used in volumetric analysis for the estimation of ferric iron, which is reduced to ferrous iron, and also for the analysis of a number of colouring matters.[2]

Double compounds of titanium trichloride with the chlorides of rubidium and cæsium have been prepared,[3] having the compositions $TiCl_3,2RbCl,H_2O$ and $TiCl_3,2CsCl,H_2O$.

Titanium Tetrachloride, $TiCl_4$.—Metallic titanium does not combine with chlorine at the ordinary temperature, but when heated it burns in the gas with brilliancy, forming the tetrachloride (Wöhler). According to Friedel and Guérin, titanium dioxide is converted in presence of chlorine at a white heat into titanium tetrachloride, oxygen being evolved. The tetrachloride is readily obtained by passing dry chlorine over a heated mixture of titanium dioxide and carbon, whilst it is also formed, together with carbonic oxide and hydrogen chloride, when chloroform vapour is passed over heated titanium dioxide.[4]

It may also be obtained by heating powdered ferrotitanium in a current of chlorine or by treating ferrotitanium with hydrochloric acid to dissolve out most of the iron, and heating the dried residue of titanic oxide with carbon in a stream of chlorine.[5] It is

[1] Polidori, *Zeit. anorg. Chem.*, 1899, **19**, 306; Stähler, *Ber.*, 1904, **37**, 4405; Spence and Son, German Patent, 154,542.

[2] Knecht, *Ber.*, 1903, **36**, 166; Knecht and Hibbert, *ibid.*, 1903, **36**, 1549; 1905, **38**, 3318; 1907, **40**, 3819; 1910, **43**, 3455.

[3] Stähler, *Ber.*, 1904, **37**, 4405. [4] Renz, *Ber.*, 1906, **39**, 249.

[5] Vigouroux and Arrivant, *Bull. Soc. chim.*, 1907, [4], **1**, 19.

a mobile, transparent, colourless liquid, having a specific gravity of 1·7604 at 0° (Pierre). It freezes [1] at—23°, and boils at 136·4° (134·8°, Emich), its vapour having the normal specific gravity of 6·836 (Dumas). It possesses a penetrating acid smell, and emits dense white fumes on exposure to air.

Titanium tetrachloride is decomposed by an excess of water with formation of titanic acid, which remains dissolved in the aqueous hydrochloric acid simultaneously formed. By careful addition of water it is possible to replace the chlorine atoms one by one by hydroxyl, yielding the compounds $TiCl_3(OH)$, $TiCl_2(OH)_2$, and $TiCl(OH)_3$.

Titanium tetrachloride yields a large number of crystalline compounds with other chlorides, analogous to those formed by stannic chloride.[2] When dry ammonia gas is passed over titanium tetrachloride it is rapidly absorbed, and a very hygroscopic powder, $TiCl_4,4NH_3$, is formed which when ignited yields a yellow sublimate of $TiCl_4,3NH_4Cl$. Other compounds with ammonia [3] have been prepared of the formulæ $TiCl_4,6NH_3$ and $TiCl_4,8NH_3$; these are solid bodies which lose ammonia readily in air and on extracting with liquid ammonia yield ammonium chloride and a dark yellow substance, *titanamide*, $Ti(NH_2)_4$.

Titanium Oxychloride, $Ti_2O_2Cl_2$, is obtained, together with the trichloride, when a mixture of hydrogen and the vapour of titanium tetrachloride is passed over the ignited dioxide. It forms reddish-brown translucent crystals, which burn when heated in the air with formation of the dioxide and the tetrachloride (Friedel and Guerin). Other oxychlorides also have been prepared.

Titanium Tribromide, $TiBr_3,6H_2O$, is obtained in unstable, deliquescent, violet-coloured crystals when a solution of titanium tetrabromide in hydrobromic acid is electrolysed, and the liquid then saturated with hydrobromic acid gas.[4]

Titanium Tetrabromide, $TiBr_4$, is obtained when hydrobromic acid is passed over the chloride [5] as an amber-yellow hygro-

[1] Emich, *Monatsh.*, 1904, **25**, 907.

[2] See Rosenheim, and Schütte, *Zeit. anorg. Chem.*, 1901, **26**, 239; Ruff and Ipsen, *Ber.*, 1903, **36**, 1777.

[3] Stähler, *Ber.*, 1905, **38**, 2619. See also Rosenheim and Schütte, *Zeit. anorg. Chem.*, 1901, **26**, 239.

[4] Stähler, *Ber.*, 1904, **37**, 4405.

[5] Thorpe, *Journ. Chem. Soc.*, 1885, **47**, 126.

scopic, finely crystalline mass which has a specific gravity of 2·6, melts at 39°, and boils at 230°.[1]

Titanium Tri-iodide, $TiI_3,6H_2O$.—Deliquescent, violet crystals of this composition are formed by the electrolytic reduction of a solution of the tetra-iodide in hydriodic acid.[2]

Titanium Tetra-iodide, TiI_4, is produced when iodine vapour is passed over heated titanium (Weber); also when dry hydriodic acid is passed into titanium tetrachloride, which is gradually heated up to its boiling point. The small quantity of free iodine giving a violet tinge may be removed by three or four distillations in a stream of hydrogen (Hautefeuille). A third process consists in passing the vapour of titanium tetrachloride mixed with hydrogen and iodine vapour through a tube heated to redness. Titanium tetra-iodide forms a brittle mass having a reddish-brown colour and metallic lustre. It melts at 150° to a yellowish-brown liquid, which solidifies on cooling in fine octahedral crystals. It distils without decomposition at a temperature slightly above 360°, giving rise to orange-coloured vapours. The specific gravity of its vapour at 440° has the normal value of 18·054. It fumes strongly in the air and dissolves readily in water.

Titanium and Sulphur.

378 Titanium combines with sulphur to form the sulphides, TiS_2, Ti_2S_3, and TiS, corresponding to the oxides of the metal.

Titanium Disulphide, TiS_2, is obtained by passing a mixture of titanium tetrachloride vapour and sulphuretted hydrogen through an ignited tube, and forms large brass-yellow lustrous scales, closely resembling mosaic gold. It burns when ignited in the air, yielding titanium dioxide and sulphur dioxide.

Titanium Sesquisulphide, Ti_2S_3, is formed by passing a mixture of moist sulphuretted hydrogen and carbon disulphide vapour over titanium dioxide heated to bright redness,[3] or by igniting the disulphide in a current of an indifferent gas;[4] it forms a greenish-black or grey powder.

Titanium Monosulphide, TiS, is prepared by heating either of the foregoing compounds in a current of hydrogen and is a lustrous substance resembling bismuth.

[1] Duppa, *Proc. Roy. Soc.*, 1857, **8**, 42. [2] Stähler, *Ber.*, 1904, **37**, 4405.
[3] Thorpe, *Journ. Chem. Soc.*, 1885, **47**, 491.
[4] von der Pfordten, *Annalen*, 1886, **234**, 290.

Titanium Sesquisulphate, $Ti_2(SO_4)_3,8H_2O$, is obtained by dissolving the metal in dilute sulphuric acid. The violet solution on concentration assumes a fine blue lustre and deposits small tufts of crystals (Glatzel).[1] By repeated evaporation in vacuo of a solution of titanium trichloride with dilute sulphuric acid, violet crystals of the composition $3Ti_2(SO_4)_3,H_2SO_4,25H_2O$ are obtained, and the same compound is formed also by the electrolysis of a solution of titanium tetrachloride in concentrated sulphuric acid. This substance forms a violet solution in water, and on repeated evaporation with concentrated sulphuric acid in absence of air, yields the anhydrous sesquisulphate as an insoluble green crystalline powder (Stähler). Titanium sesquisulphate is decomposed by heat into sulphur dioxide, sulphur trioxide, and titanium dioxide. It forms an alum with cæsium sulphate, $Cs_2SO_4,Ti_2(SO_4)_3,24H_2O$, which crystallises in cubes, and a similar alum with rubidium sulphate,[2] whilst a double sulphate, $Ti_2(SO_4)_3,Na_2SO_4,5H_2O$, has also been prepared.[3] The violet acid salt forms with rubidium and ammonium sulphates the compounds $3Ti_2(SO_4)_3,Rb_2SO_4,24H_2O$ and $3Ti_2(SO_4)_3,(NH_4)_2SO_4,18H_2O$ (Stähler).

Normal Titanium Disulphate, $Ti(SO_4)_2,3H_2O$, is formed by the oxidation of the sesquisulphate with nitric acid, and on evaporation remains as a transparent yellowish deliquescent amorphous mass. The sulphate forms double salts, such as $K_2SO_4,Ti(SO_4)_2,3H_2O$; $Ti(SO_4)_2,CaSO_4$, etc.[4]

Basic Titanium Sulphate, $(TiO)SO_4$, is obtained as a hard white mass by dissolving dry titanic acid in boiling sulphuric acid and evaporating,[5] whilst crystals of $(TiO)SO_4,5H_2O$ are obtained by boiling titanic acid with alcoholic sulphuric acid and evaporating.[6] Several other basic sulphates have been prepared[7] by heating titanium dioxide with sulphuric acid in sealed tubes at different temperatures.

[1] Compare Stähler, *Ber.*, 1905, **38**, 2619.
[2] Piccini, *Gazz.*, 1895, **25** (ii.), 542; *Zeit. anorg. Chem.*, 1898, **17**, 355.
[3] Spence and Son, German Patent, 149602 (1904).
[4] Weinland and Kühl, *Zeit. anorg. Chem.*, 1907, **54**, 253.
[5] Merz, *J. pr. Chem.*, 1866, **99**, 157.
[6] Rosenheim and Schütte, *Zeit. anorg. Chem.*, 1901, **26**, 239.
[7] Blondel, *Bull. Soc. chim.*, 1899, [3], **21**, 262.

Titanium and Nitrogen.

379 Titanium is one of the elements which very readily combine with nitrogen, and several compounds of these two elements are known.

Normal Titanium Nitride, Ti_3N_4, is obtained as a copper-coloured substance by heating ammonio-chloride of titanium, $TiCl_4,4NH_3$, by itself (H. Rose), or better in a stream of ammonia gas.[1] This was originally supposed to be metallic titanium, but Wöhler [2] proved that it consisted of a nitride of titanium having the above composition.

Titanium Dinitride, TiN_2, is obtained as a dark-blue powder, having a copper-red lustre, resembling sublimed indigo, by strongly igniting titanium dioxide in a current of ammonia gas (Wöhler).

Titanium Mononitride, TiN or Ti_2N_2, is obtained by heating titanium dioxide very strongly in the electric furnace in presence of nitrogen, and is a bronze-yellow mass which has a specific gravity of 5·18 and is hard enough to scratch rubies and cut diamonds.[3]

Titanium and Carbon.

380 *Titanium Carbide*, TiC, is prepared by fusing titanium dioxide with an excess of carbon, or with calcium carbide in the electric furnace, and is thus obtained as a mass having a crystalline fracture, and a specific gravity of 4·25; it is not attacked by hydrochloric acid, is only slowly dissolved by aqua regia, and does not decompose steam at 700°. In other respects it closely resembles metallic titanium, but burns more readily in oxygen.[4]

Steel-grey crystals of titanium carbide have also been obtained from cast iron prepared from ores containing titanium.[5] Titanium carbide is used for making arc lamp electrodes.

Titanium Cyanonitride.—When iron ores containing titanium are reduced in the blast-furnace small brilliant copper-coloured cubes, which are hard enough to scratch glass and are almost infusible, are found in cavities both of the slag and of the metal.

[1] Liebig, *Pogg. Ann.*, 1830, **21**, 259. [2] *Annalen*, 1850, **73**, 34.
[3] Moissan, *Compt. rend.*, 1895, **120**, 290.
[4] Moissan, *Compt. rend.*, 1895, **120**, 290; 1897, **125**, 839.
[5] Shimer, *Chem. News*, 1887, **55**, 156.

A mass containing as much as 80 lbs. has been found in a single blast-furnace in the Harz. This substance was examined by Wollaston in 1822 and believed by him to be metallic titanium ;[1] but Wöhler in 1849 showed that it contained nitrogen and cyanogen, and gave to it the formula $Ti(CN)_2,3Ti_3N_2$. He likewise obtained it artificially[2] by heating a mixture of ferrocyanide of potassium and titanium dioxide in a well-closed crucible at a temperature sufficient to melt nickel. Titanium cyanonitride can also be prepared by heating to whiteness a mixture of titanium dioxide and charcoal in a tube of gas carbon in a stream of dry nitrogen (Deville and Wöhler).[3] A third method of preparation is to fuse potassium cyanide in the vapour of titanium tetrachloride (Wöhler). It has a specific gravity of 5·28, and is attacked only by a mixture of nitric and hydrofluoric acids. When ignited in a current of steam it is decomposed as follows :

$$Ti(CN)_2,3Ti_3N_2+20H_2O=2HCN+10TiO_2+6NH_3+10H_2.$$

Chlorine also decomposes this substance at a red heat, titanium tetrachloride and a volatile sublimate consisting of a compound of titanium tetrachloride and cyanogen chloride being formed. When fused with potash ammonia is given off, potassium titanate being produced.

Detection and Estimation of Titanium.

381 Titanium is distinguished from tin inasmuch as its oxides are not reduced to the metallic state when heated on charcoal before the blowpipe. With microcosmic salt titanium dioxide yields a colourless bead in the outer flame, but in the inner flame the bead is yellow whilst hot and assumes a violet colour on cooling. According to Riley the delicacy of this reaction is increased by melting metallic zinc in the microcosmic bead heated on charcoal, a distinct coloration being then obtained when the zinc is burnt away, even with minute quantities of titanium. When fused in the microcosmic bead with addition of a small quantity of an iron salt in the reducing flame, a bright-red bead is obtained. Titanium compounds do not colour the gas-flame, but both the spark and the arc spectrum

[1] *Phil. Trans.*, 1823, **113**, 17. [2] *Annalen*, 1850, **73**, 34 ; **74**, 212.
[3] *Annalen*, 1857, **103**, 230.

show an enormous number of bright lines, chiefly in the blue and green, which have been carefully mapped by Thalén and others.

Metallic zinc placed in a hydrochloric acid solution of titanic acid evolves hydrogen and the liquid assumes a violet-blue colour; a dark violet precipitate is formed if the solution be not too dilute, and this gradually turns white by oxidation. The violet-blue solution when diluted with water assumes a rose-colour, and this reaction serves for the detection of small quantities of titanium. Sodium thiosulphate when boiled with a nearly neutral solution of a titanate precipitates the whole of the titanic acid, and this reaction serves as a means of separating titanium from iron and the metals of the cerium group.

In order to remove silica, when present, the mixture is evaporated with hydrofluoric acid, the silicon being expelled as silicon tetrafluoride.

Titanium is always estimated gravimetrically in the form of titanium dioxide, this being thrown down from its solutions in acids by ammonia, or by saturating with sulphur dioxide and boiling. Titanium may also be estimated volumetrically by reducing titanium dioxide to titanium sesquioxide by means of zinc in an acid solution and subsequently oxidising with standard permanganate.

Atomic Weight of Titanium.—The atomic weight of titanium was first determined by Rose [1] in 1829 by decomposing titanium tetrachloride with water, weighing the titanic acid formed and estimating the chlorine in the filtrate, the number found being 47·72. A redetermination was made in 1885 by Thorpe,[2] who analysed pure titanium tetrachloride and tetrabromide, the amount of silver required for complete precipitation of the halogen, the amount of silver halide formed, and the quantity of titanium dioxide yielded by each being ascertained; the average of the results of the six series of experiments gave the number 48·1, which is at present (1913) adopted.

[1] *Pogg. Ann.*, 1829, **15**, 145. [2] *Journ. Chem. Soc.*, 1885, **47**, 108.

ZIRCONIUM. Zr. = 90·6.

382 In 1789 Klaproth found a new earth in the mineral zircon, to which he gave the name of zirconia. He discovered in 1795 that the same earth was contained in hyacinth, a mineral found in Ceylon, and he thus ascertained the truth of Werner's previous supposition that these two minerals were identical. Zircon and hyacinth possess the formula $ZrSiO_4$, and are more or less coloured by ferric oxide. Zirconium is likewise found in a few other rare minerals, and occurs in appreciable quantities in Norwegian granite, together with thorium and several of the rare earths.[1]

The metal zirconium was first obtained by Berzelius in the form of an iron-grey powder by heating potassium zirconofluoride with potassium. The metal can also be obtained, according to Troost, by passing the vapour of zirconium chloride, $ZrCl_4$, over heated sodium. The ignited amorphous metallic powder thus obtained is so finely divided that it passes through the pores of filter paper, but it assumes a metallic lustre under the burnisher. The amorphous metal may also be prepared by heating zirconia with magnesium powder,[2] and thus prepared it has a velvet-black appearance like wood charcoal.

Wedekind[3] has obtained a metal containing 99·09 per cent. of zirconium. He heats an intimate mixture of ZrO_2 and calcium shavings in an evacuated iron vessel. When the reaction is completed the contents of the tube are treated successively with water, acetic acid, dilute hydrochloric acid, and water, all the operations being conducted in absence of air. The residual powder is then washed with acetone and dried in vacuo at 250–300°; finally, at a temperature of 800–1000°, the powder sinters, but does not melt; it exhibits a mirror-like brilliancy on polishing.

Crystallised zirconium was first obtained by heating potassium zirconofluoride with aluminium at the temperature of melting iron; it is, however, best prepared by heating zirconia in the electric furnace with an insufficient quantity of carbon for its complete reduction, and is thus obtained as a metallic button con-

[1] Phipson, *Chem. News*, 1896, **73**, 145.

[2] Phipson, *Compt. rend.*, 1865, **61**, 745; *Chem. News*, 1906, **93**, 119; Winkler, *Ber.*, 1890, **23**, 2664.

[3] *Annalen*, 1913, **395**, 149; compare also Weiss and Neumann, *Zeit. anorg. Chem.*, 1910, **65**, 248.

taining some zirconia but free from carbon and nitrogen. It may also be obtained by heating the carbide with zirconia in a similar manner,[1] or by heating potassium zirconofluoride with magnesium in the electric furnace.[2]

Crystallised zirconium forms broad, apparently monoclinic, plates, has a specific gravity of 4·08 at 15°,[3] and is hard enough to scratch glass and rubies. It is only very slowly oxidised in the air even at a white heat, but burns in the oxy-hydrogen flame, and yields the chloride when heated to dull redness in chlorine or hydrogen chloride It is also dissolved by caustic potash with evolution of hydrogen. It is only slowly attacked by acids, with the exception of hydrofluoric, even on heating, but is rapidly oxidised by aqua regia. The amorphous metal readily takes fire in the air on warming.

ZIRCONIUM COMPOUNDS.

383 *Zirconium Oxide or Zirconia*, ZrO_2.—In order to prepare this oxide zircon is ignited and then quenched in water. The powdered mineral is mixed with three to four times its weight of acid potassium fluoride, and gently heated in a platinum vessel until all moisture has been driven off. The platinum crucible is then placed in a Hessian one, and both are well covered and exposed for two hours to the strongest heat of a wind furnace. The porcelain-like mass thus obtained is boiled with water containing hydrofluoric acid, and the insoluble potassium silicofluoride filtered off. On cooling the solution, crystals of potassium zirconofluoride are deposited, and these are purified by recrystallisation. The pure salt is then heated with sulphuric acid until all the hydrofluoric acid is driven off; the residue is dissolved in water, and the zirconia precipitated in the cold by ammonia.[4]

In order to avoid the use of hydrofluoric acid, the very finely powdered zircon may be treated as follows. It is first fused with hydrogen potassium sulphate and the fused mass repeatedly boiled out with water containing sulphuric acid when a residue of basic zirconium sulphate, $4ZrO_2,3SO_3,14H_2O$, is obtained,

[1] Moissan, *Compt. rend.*, 1893, **116**, 1222; Troost, *ibid.*, 1428.
[2] Wedekind, *Zeit. Elektrochem.*, 1904, **10**, 331.
[3] Meyer, *Monatsh.*, 1899, **20**, 793.
[4] Homberger, *Annalen*, 1876, **181**, 232.

which is next fused with caustic soda in a silver basin. This is then lixiviated with water, the residual zirconia, which contains soda, washed with hot water and dissolved in hot concentrated sulphuric acid, the solution filtered and precipitated with ammonia.[1] The precipitate thus obtained consists of zirconium hydroxide, which readily parts with its water on heating. When heated at 140—200° it has the composition ZrO_2,H_2O, and is known as zirconic acid. A hydrated oxide containing less water than this is obtained by repeatedly boiling zirconium oxychloride with water and drying the precipitate at 100°; this has been called metazirconic acid.[2] According to van Bemmelen,[3] however, these substances are probably not true hydroxides, but colloidal zirconia, containing water in the form of a hydrogel. The hydroxide is slightly soluble in water, and colours yellow turmeric paper brown. When precipitated and washed in the cold, it is easily soluble in dilute acids; if, however, it be precipitated from a hot solution, or washed with boiling water, it is soluble only in concentrated acids. When heated to incipient redness it is converted into zirconia with evolution of heat. The oxide thus obtained has the specific gravity[4] 5·489, and is only slightly soluble even in hydrofluoric acid, but dissolves on heating in a mixture of two parts of sulphuric acid and one part of water.

Zirconia can be obtained in the crystalline state in the form of tetragonal prisms isomorphous with cassiterite and rutile and having a specific gravity of 5·71.[5] For this purpose the amorphous oxide is fused with borax in a porcelain furnace, the fused residue being boiled out with sulphuric acid.

Zirconia is employed in the preparation of rods for the Nernst electric lamp.

The linear coefficient of expansion is $\alpha = 0{\cdot}00000084$, very nearly the same as fused quartz. Crucibles, etc., can be made by mixing zirconia with 10 per cent. of magnesia. Platinum can be liquefied in such crucibles with the oxyhydrogen flame. Quartz can also be melted without destroying the crucible.[6]

Zirconia, like the dioxides of the other metals of this group,

[1] Franz, *Ber.*, 1870, **3**, 58.
[2] Ruer, *Zeit. anorg. Chem.*, 1905, **43**, 282.
[3] *Zeit. anorg. Chem.*, 1906, **49**, 125.
[4] Venable and Belden, *J. Amer. Chem. Soc.*, 1898, **20**, 273.
[5] Nordenskiold, *Pogg. Ann.*, 1861, **114**, 612.
[6] Weiss and Lehmann, *Zeit. anorg. Chem.*, 1909, **65**, 178.

acts as an acid-forming oxide, and yields salts corresponding to the metasilicates and metatitanates.

Sodium Zirconate, Na_2ZrO_3, obtained by fusing the oxide with sodium carbonate, forms a crystalline mass which is decomposed by water with separation of zirconia. When heated with an excess of sodium carbonate to whiteness the salt Na_4ZrO_4 is produced. This is again decomposed by water with formation of hexagonal tablets having the composition $Na_2Zr_8O_{17},12H_2O = Na_2O,8ZrO_2,12H_2O$.

The zirconates of calcium and magnesium are crystalline and insoluble in water.

Zirconium Peroxide, $Zr_2O_5,9H_2O$, is obtained as a white powder when hydrogen peroxide is added to a solution of zirconium sulphate. Under certain conditions a hydrated oxide $ZrO_3,5H_2O$ is formed,[1] and this when treated with excess of hydrogen peroxide and an alkali hydroxide is stated to form the alkali salts of *perzirconic acid*,[2] $H_4Zr_2O_{11}$.

Zirconium and Hydrogen.—When zirconia is heated with magnesium powder in a current of hydrogen the latter is absorbed, the product containing probably zirconium hydride, ZrH_2, together with zirconia and perhaps a lower oxide.[3] The hydride is also formed when hydrogen acts on the metal at a red heat.[4]

Zirconium Fluoride, ZrF_4, is obtained by heating zirconia with acid ammonium fluoride. The residual mass is easily soluble in water containing hydrofluoric acid, and crystallises in glistening triclinic tablets having the composition $ZrF_4,3H_2O$.

Zirconium fluoride forms a series of double salts with other fluorides, which are isomorphous with the corresponding silicofluorides, titanifluorides, and stannifluorides.

Potassium Zirconofluoride, K_2ZrF_6, is obtained by igniting zircon with acid potassium fluoride or by pouring a solution of potassium fluoride into an excess of zirconium fluoride solution. It crystallises from hot water in small acute rhombic prisms, and dissolves at 2° in 128, at 15° in 71, and at 100° in 4 parts of water.

When zirconium hydroxide is dissolved in the smallest quantity of hydrofluoric acid, and the liquid is poured into a

[1] Bailey, *Journ. Chem. Soc.*, 1886, **49**, 481.
[2] Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 609.
[3] Winkler, *Ber.*, 1891, **24**, 888.
[4] Weiss and Neumann, *Zeit. anorg. Chem.*, 1910, **65**, 248.

concentrated solution of neutral potassium fluoride, the salt K_2ZrF_6,KF is precipitated, and crystallises from boiling water in fine needles.

If sodium fluoride and zirconium fluoride are mixed in any proportion, the salt $Na_2ZrF_6,4NaF$ is produced. It forms small monoclinic crystals which dissolve in 258 parts of water at 18°, and at 100° in about 60 parts of water.

Ammonium salts, corresponding to the salts of potassium, and other double fluorides,[1] are known, which crystallise well and are usually soluble.

Zirconium Chloride, $ZrCl_4$, is obtained by passing chlorine gas over a heated mixture of zirconia and charcoal, or by the action of chlorine or hydrogen chloride on the heated metal, when it is obtained as a white, crystalline sublimate. It may be recrystallised from hydrochloric acid, but it is doubtful whether it has ever been obtained in this way free from the oxychloride. Zirconium chloride forms with ammonia the compounds[2] $ZrCl_4,8NH_3$ and $ZrCl_4,3NH_3$. On addition of water to the chloride heat is evolved, and zirconium oxychloride, $ZrOCl_2$, is formed, which remains dissolved in the acid solution. The same compound is obtained by dissolving zirconium hydroxide in dilute hydrochloric acid, and on evaporation crystallises out in prismatic needles belonging to the tetragonal system, and having the composition $ZrOCl_2,8H_2O$.[3] These are readily soluble in water, have an astringent taste, and when heated to 50° lose water, forming more basic oxychlorides, whilst by treatment with concentrated hydrochloric acid crystals of $ZrOCl_2,6H_2O$ and $ZrOCl_2,3H_2O$ have been obtained.[4]

Zirconium Bromide, $ZrBr_4$, is prepared in a similar way to the chloride, and forms a white crystalline powder which is easily volatilised at the temperature of the gas flame. In contact with moist air or water it forms zirconium oxybromide, $ZrOBr_2$, which crystallises in needles, and may also be prepared by evaporating a solution of the hydroxide in hydrobromic acid, when $ZrOBr_2,8H_2O$ separates out.[5] With ammonia,[6]

[1] See also Wells and Foote, *Zeit. anorg. Chem.*, 1895, **16**, 434; *Amer. J. Sci.*, 1897, **3**, 461.

[2] Stähler and Denk, *Ber.*, 1905, **38**, 2611; compare Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 815.

[3] Weibull, *Ber.*, 1887, **20**, 1394.

[4] Venable and Baskerville, *J. Amer. Chem. Soc.*, 1898, **20**, 321.

[5] Rosenheim and Frank, *Ber.*, 1907, **40**, 803.

[6] Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 839; Stähler and Denk, *Ber.*, 1905, **38**, 2611.

zirconium bromide gives the compounds $ZrBr_4,4NH_3$ and $ZrBr_4,10NH_3$.

Zirconium Iodide, ZrI_4, is obtained by passing hydrogen iodide over zirconium or the carbide at a bright red heat. According to Dennis and Spencer,[1] it is a white, crystalline body which is insoluble in water and acids; Stähler and Denk,[2] however, state that it dissolves in water and acids, the aqueous solution depositing crystals of the *oxyiodide*, $ZrOI_2,8H_2O$, when evaporated.

Zirconium Sulphide.—When metallic zirconium and sulphur are heated together in a current of hydrogen they combine with evolution of heat to form a cinnamon-brown powder, which assumes a metallic lustre under the burnisher. This is not attacked by most of the dilute acids, but dissolves slowly in aqua regia and readily in hydrofluoric acid. When fused with potash, zirconia and potassium sulphide are formed.

Zirconium Sulphate, $Zr(SO_4)_2$, is obtained by dissolving the oxide or hydroxide in sulphuric acid, evaporating, and heating nearly to redness. It is a white mass which dissolves slowly but completely in cold, and quickly in hot water. Hydrated crystals are obtained by concentrating a solution which contains free acid, and these swell up on heating, like alum. The salt decomposes at a red heat, leaving a residue of pure zirconia. The behaviour of zirconium sulphate in solution[3] is best represented by the formula $(ZrO)SO_4,H_2SO_4$, whilst the crystalline hydrated salt is $(ZrO)SO_4,H_2SO_4,3H_2O$ and not $Zr(SO_4)_2,4H_2O$, as was formerly thought. If its solution be saturated with zirconium hydroxide a basic salt, $Zr(SO_4)_2,ZrO_2$ or $(ZrO)SO_4$, is formed, and this is obtained on evaporation as a hydrated mass. If the normal salt be precipitated with alcohol an insoluble salt, $Zr(SO_4)_2,2ZrO_2$, is thrown down.

Zirconium and Nitrogen.—The nitride Zr_2N_3 is obtained by heating zirconium chloride to redness in a current of dry ammonia,[4] and also by heating zirconia and magnesium in a loosely-covered crucible.[5] It is a brownish-green, crystalline powder which oxidises with incandescence when gently heated in air (Wedekind). A nitride of the formula Zr_3N_8 is formed

[1] *J. Amer. Chem. Soc.*, 1896, **18**, 673.

[2] *Ber.*, 1904, **37**, 1137.

[3] Ruer, *Zeit. anorg. Chem.*, 1904, **42**, 187; Ruer and Levin, *ibid.*, 1905, **46**, 449; Rosenheim and Frank, *Ber.*, 1907, **40**, 803.

[4] Matthews, *J. Amer. Chem. Soc.*, 1898, **20**, 840.

[5] Wedekind, *Zeit. anorg. Chem.*, 1905, **45**, 385.

when the compound $ZrCl_4,8NH_3$ is heated to redness in nitrogen (Matthews).

Zirconium Nitrate, $Zr(NO_3)_4$, is obtained as a yellow gummy mass by dissolving the hydroxide in nitric acid and evaporating at a moderate heat. If the solution be evaporated in vacuo over caustic soda and phosphorus pentoxide, extremely hygroscopic crystals of $Zr(NO_3)_4,5H_2O$ separate out.[1]

Zirconium Boride, Zr_3B_4, has been prepared by heating in the electric furnace a mixture of zirconium and boron;[2] it forms a steel-grey mass, consisting of microscopic crystals, and has the specific gravity 3·7.

Zirconium Carbides.—Zirconium combines with carbon to form two carbides having the composition ZrC_2 and ZrC. The *dicarbide* is obtained by heating zirconia with an excess of carbon in the the electric furnace and has a metallic appearance and brilliant fracture, and is not decomposed by water even on heating. The *monocarbide* is prepared in a similar manner, but the mixture of zirconia and carbon is placed in a carbon tube closed at one end, which is then heated in the electric furnace. It has a grey colour and metallic lustre, and is hard enough to scratch quartz. It is permanent in the air and is not decomposed by water, but burns brilliantly when heated strongly in oxygen.[3]

Zirconium Silicide, $ZrSi_2$.—This compound is obtained by heating a mixture of potassium zirconofluoride, aluminium, sulphur, and sand, the whole being covered with a layer of magnesium powder.[4] It forms small steel-grey crystals having the specific gravity 4·88 at 22°.

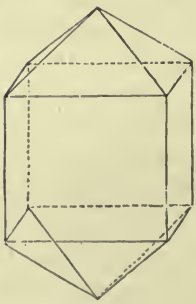


Fig. 177.

Silicates of Zirconium.—Of these, zircon or hyacinth, $ZrSiO_4$, is the most important. It occurs in crystalline rocks, especially in granular limestone, schist, gneiss, syenite, and granite. The chief localities are in alluvial sands in Ceylon, the Urals, in the Isle of Harris, in Greenland, in the gold districts of Australia, and in many places in North America. Zircon crystallises in tetragonal prisms and pyramids (Fig. 177), having an adamantine

[1] Rosenheim and Frank, *Ber.*, 1907, **40**, 803.
[2] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 14.
[3] Moissan, *Compt. rend.*, 1893, **116**, 1222; 1896, **122**, 651.
[4] Hönigschmid, *Compt. rend.*, 1906, **143**, 224.

lustre; they are colourless in the pure state. Usually, however, zircon is coloured red or yellow by ferric oxide. The colourless and smoke-coloured varieties are termed jargon. This variety exhibits a peculiar absorption spectrum, from which Sorby concluded that it contained a new element; to this he gave the name of jargonium, but subsequently he found that these lines were caused by the presence of uranium oxide. An artificial jargon yielded a similar spectrum, though neither uranium nor zirconium compounds do so.[1]

Detection and Estimation of Zirconium.

384 The reactions of the zirconium salts are very similar to those of the metals contained in cerite and gadolinite. A reaction of zirconium by which it is distinguished from the cerium metals is the formation of a basic potassium zirconium sulphate, insoluble in water and hydrochloric acid. This salt is obtained by adding a hot solution of potassium sulphate to a concentrated solution of a zirconium salt. This reaction also serves to separate zirconium from titanium, tantalum, and columbium. Another method of separating zirconium from the metals of the cerium and iron groups is to boil the solution with sodium thiosulphate, when zirconium alone is precipitated as the thiosulphate; this on washing and heating leaves a residue of zirconia.

Titanic acid and thoria are also precipitated together with the zirconia by sodium thiosulphate. In order to separate these ammonium oxalate is added to the hydrochloric acid solution, when the thoria is thrown down. Ammonium carbonate is now added to the filtered liquid, when, in the presence of the oxalate, only titanic acid is precipitated, the zirconia remaining in solution (Hermann). Zirconium can readily be separated from iron, titanium, &c., by means of hydrogen peroxide; this precipitates it quantitatively from solutions of the sulphate as the hydrated peroxide (Bailey).

The spectrum of zirconium has been mapped by Thalén, and contains characteristic lines in the red and blue.

Atomic Weight of Zirconium.—The first accurate determination of the atomic weight of zirconium is that of Marignac,[2] who from the analysis of potassium zirconofluoride obtained the

[1] *Chem. News*, 1870, **21**, 73.
[2] *Ann. Chim. Phys.*, 1860, [3], **60**, 257.

number 90·03. Bailey,[1] from the weight of zirconia yielded by a known quantity of pure zirconium sulphate, found the number 90·65, whilst Venable,[2] who estimated the zirconia obtained by heating the oxychloride, $ZrOCl_2,3H_2O$, found the number 90·78. The atomic weight now (1913) adopted is 90·6.

THORIUM. Th. = 232·4.

385 In the year 1815 Berzelius believed that he had found in several Swedish minerals a new earth to which he gave the name of thoria, but on further examination the substance turned out to be basic phosphate of yttrium. On the other hand, in 1828,[3] he discovered a distinct earth in a mineral from the island of Lövön, in Norway, now termed thorite, and to this the name of thoria was given, as it agreed in many of its properties with the substance previously so named. Besides being found in thorite, this substance was discovered in other rare minerals; thus by Wöhler in pyrochlor, by Bergman and others in orangite, and by Karsten in monazite, a phosphate of cerium and lanthanum which contains 4–18 per cent. of thoria. Another source of thoria is the mineral euxinite from Arendal, in which this earth was discovered by Mosander and Chydenius, and it has also been found in Norwegian granite.[4] More recently it has been discovered in a mineral called thorianite occurring in Ceylon, which contains 70–80 per cent. of thoria, along with 11–15 per cent. (UO_2+UO_3), 2–3 per cent. of lead, and varying amounts of metals of the cerium and ytterbium group and SiO_2 and CaO.[5] This mineral also contains helium, and when heated to redness evolves 9 c.c. of this gas per 1 gram.[6]

The following table gives the composition of some of these minerals.[7]

[1] *Proc. Roy. Soc.*, 1890, **46**, 74.

[2] *J. Amer. Chem. Soc.*, 1898, **20**, 119.

[3] *Pogg. Ann.*, 1829, **16**, 385.

[4] Phipson, *Chem. News*, 1896, **73**, 145.

[5] Dunstan, *Nature*, 1904, **69**, 510; Dunstan and Blake, *Proc. Roy. Soc.*, 1905, **76A**, 253.

[6] Ramsay, *J. Chim. phys.*, 1905, **3**, 617.

[7] See Schilling, *Zeit. angew. Chem.*, 1902, **15**, 921, where a résumé of the analyses of orangite and thorite is given.

Thorite from Lövön.		Thorianite.		Monazite from Ilmengebirge.	
SiO_2	19·31	ThO_2	78·86	P_2O_5	28·50
ThO_2	58·91	UO_2	6·03	ThO_2	17·95
UO_3	1·64	UO_3	9·07	SnO_2	2·10
Fe_2O_3	3·46	CeO_2, La_2O_3, Di_2O_3	1·02	Ce_2O_3	26·00
Mn_2O_3	2·43			La_2O_3	23·40
CuO	2·62			MnO	1·86
MgO	0·36	PbO	2·59	CaO	1·68
K_2O	0·15	Fe_2O_3	0·46		
Na_2O	0·11	CaO	1·13		101·49
PbO	0·82	He	0·39		
SnO_2	0·01	P_2O_5	trace		
Al_2O_3	0·06	Insol. in HNO_3	0·20		
H_2O	9·66				
	99·54		99·75		

Thorium occurs also in other minerals containing the metals of the cerium group, as gadolinite and orthite. In one of these minerals Bahr believed he had found another new metal to which he gave the name wasium, but he afterwards convinced himself that this substance is identical with thorium.[1]

Doubts have been put forward as to the individuality of thorium, and Baskerville,[2] from experiments on the fractional distillation of the chloride in a current of chlorine, concludes that it contains two other elements to which he gives the names berzelium and carolinium. The work of other investigators, however, does not confirm this result, but points to the uniform nature of thorium.[3]

At the present time thorium compounds are prepared on the manufacturing scale, as they form the chief constituent of the mantles employed for the Welsbach incandescent gas-burner; they are put on the market chiefly in the form of crude thorium nitrate which contains also the nitrates of zirconium and the cerite earths. Thorite is the most convenient raw material, but is not found in sufficient quantity, and the crude material mostly employed is the Brazilian or American monazite sand, which has been formed by disintegration of the rock containing the mineral monazite.

[1] *Annalen*, 1864, **132**, 227.

[2] Baskerville, *J. Amer. Chem. Soc.*, 1901, **23**, 761; 1904, **26**, 922: *Ber.*, 1905, **38**, 1444; see also Brauner, *Proc. Chem. Soc.*, 1901, **17**, 67.

[3] Meyer and Gumprey, *Ber.*, 1905, **38**, 817; Eberhard, *ibid.*, 826.

Although the process adopted for the preparation on a large scale of thorium nitrate for the incandescent mantle industry is kept secret, the following is a general outline. The powdered monazite sand either from Brazil or Carolina is moderately heated with concentrated sulphuric acid in cast-iron pans. When the reaction is finished the partially solidified product is dissolved in cold water. It is important that at this stage the solution be kept strongly acid, otherwise the phosphates of the metals will be deposited. The undissolved residue of quartz, ferrotitanium, zircon, magnetic oxide of iron, etc., is separated by decantation.

The solution is now fractionally neutralised with magnesia. Owing to thorium phosphate being the least soluble of the phosphates, the first fraction consists mainly of this.

The crude phosphate is dissolved in concentrated hydrochloric acid, oxalic acid added, when the thorium is precipitated as oxalate, together with small quantities of cerium and ytterbium metals. The well washed precipitate is then treated with warm sodium carbonate solution. The thorium goes into solution with traces of ytterbium metals, but the cerium remains undissolved as the double carbonate. By treatment with alkali hydroxide the hydroxide is precipitated, or the oxalate is reprecipitated by means of hydrochloric acid. In order to remove traces of impurities the oxalate or hydroxide is converted into sulphate with sulphuric acid and the sulphate purified by being several times recrystallised, the salt $Th(SO_4)_2,8H_2O$ crystallising out. In order to prepare the nitrate this salt is boiled with ammonia, by which means the hydroxide is produced. This is well washed, and dissolved in nitric acid. The solution is evaporated to dryness, and heated on the water-bath until on ignition it is found to contain 48 to 49 per cent. of ThO_2, representing the nitrate with practically $4H_2O$.[1]

Metallic Thorium is obtained by heating potassium thorium chloride with sodium in an iron cylinder. Thus prepared it forms microscopic hexagonal tablets, having the colour of nickel, and giving a silver-white streak. It has also been prepared by the action of sodium vapour on the vapour of certain volatile organic compounds of thorium such as the acetylacetonate.[2] It

[1] Boehm, *Chemische Industrie*, 1906, **29**, No. 17–19; Dieseldorff, *Chemische Industrie*, 1906, **29**, 411.

[2] Siemens and Halske, German Patent, 133959, 1900; see also Moissan and Hönigschmid, *Ann. Chim. Phys.*, 1906, [8], **8**, 182.

has a specific gravity of 11·0 (Nilson), and 11·32, but after heating and rolling 12·16 (v. Bolton), and takes fire when heated in the air, burning with a bright flame; it dissolves with difficulty in hydrochloric acid, and is not attacked by aqueous alkalis, but is readily soluble in aqua regia[1]; with nitric acid it first dissolves rapidly, but soon becomes passive. Thorium possesses the property of radio-activity, and this will be discussed in the chapter on this subject.

COMPOUNDS OF THORIUM.

386 *Thorium Dioxide* or *Thoria*, ThO_2, is obtained from thorite or orangite by heating the powdered mineral with a slight excess of sulphuric acid and a little water; the dried mass is powdered, heated to remove excess of sulphuric acid, and the residue carefully dissolved in six to seven parts of ice-cold water. The solution is filtered from silica, and heated to the boiling point with ammonia. The precipitated hydroxides are washed by decantation, dissolved in hydrochloric acid and precipitated with oxalic acid, the precipitate well washed by decantation, and ignited. The thoria thus obtained still contains ceria, yttria and a little manganese. To obtain pure thoria the product is again dissolved in sulphuric acid, the excess of sulphuric acid removed by careful heating, the powdered salt dissolved in ice-cold water, and the temperature of the solution allowed to rise gradually to 20°. A hydrated sulphate of thorium then separates out as an insoluble precipitate, the other metals remaining in solution, and by repeating the process several times the thorium sulphate may be obtained perfectly pure. It is then precipitated by ammonia and the hydroxide thus obtained ignited.[2]

Pure thoria is a snow-white powder, which may be obtained in tetragonal crystals, isomorphous with those of cassiterite and rutile, by heating the amorphous powder with borax in a porcelain furnace. They possess a specific gravity of 10·2, and dissolve in sulphuric acid only on long-continued boiling. As already mentioned, thoria forms the chief constituent of the Welsbach incandescent mantles, the other and smaller con-

[1] Nilson, *Ber.*, 1882, **15**, 2519, 2537; 1883, **16**, 153.
[2] Krüss and Nilson, *Ber.*, 1887, **20**, 1665.

stituents consisting of more basic oxides, that of cerium being usually employed (see p. 791).

Meta-thorium Oxide is obtained by igniting the oxalate, and its peculiar deportment with volatile acids explains the fact that Bahr believed this to be the oxide of a new metal. It was considered to be Th_3O_5, but has been found to have the empirical formula ThO_2, and, according to Wyrouboff and Verneuil,[1] is a polymerised form of thorium dioxide. If it be treated with hydrochloric acid or nitric acid no apparent action takes place, but if the excess of acid be evaporated on the water-bath, a brownish semi-transparent residue is left, and this dissolves in water to form a translucent opalescent liquid which appears milk-white in reflected light, and yields a precipitate with acids. This is due to the fact that the oxide forms salts with these acids without loss of water, and these are soluble in water but not in the acids, and are therefore precipitated again by addition of the acids to the solution. If the solution be treated with ammonia and the precipitate dried at 100°, a compound having the composition $Th_4O_7(OH)$ is obtained and this is insoluble in acids.[2]

Thorium Peroxide, Th_2O_7.—This unstable compound is produced when hydrogen peroxide is added to the sulphate or acetate, and then excess of ammonia added.[3] It forms a gelatinous precipitate which on keeping slowly gives up oxygen, being converted into ThO_3.[4]

Thorium Hydride, ThH_4, is obtained by heating thorium to a dull red heat in hydrogen.[5] It is not acted upon by water, but dissolves in hydrochloric acid with evolution of hydrogen.

387 *Salts of Thorium.*—The salts of thorium are colourless, and those which are soluble possess a strongly astringent taste.

Thorium Fluoride, ThF_4, is obtained by the addition of hydrofluoric acid or a fluoride to a solution of a thorium salt as a gelatinous precipitate which passes into a heavy white powder, $ThF_4,4H_2O$. The same powder is produced by the action of hydrofluoric acid on thoria. The anhydrous free product is

[1] *Compt. rend.*, 1898, **127**, 863; *Zeit. anorg. Chem.*, 1901, **28**, 90; *Ann. Chim. Phys.*, 1905, [8], **6**, 441; see also Stevens, *Zeit. anorg. Chem.*, 1901, **27**, 41.

[2] Cleve, *Bull. Soc. chim.*, 1874, **21**, 115.

[3] Wyrouboff and Verneuil, *Ann. Chim. Phys.*, 1906, [8], **6**, 441.

[4] Pissarjewski, *Zeit. angew. Chem.*, 1902, **31**, 359.

[5] Matignon and Delépine, *Compt. rend.*, 1901, **132**, 36.

obtained by leading hydrogen fluoride over anhydrous thorium chloride or bromide heated to 350–400°.[1]

Potassium Thorofluoride, $K_2ThF_6,4H_2O$, is obtained by boiling the hydroxide with potassium fluoride and hydrofluoric acid, in the form of a heavy black powder. When a solution of the chloride is precipitated with acid potassium fluoride the compound $K_2ThF_6,4ThF_4,H_2O$ is thrown down. Other double fluorides with potassium fluoride are known, but as they are all insoluble in water and hydrofluoric acid, it is impossible to tell whether they are definite compounds or mixtures of the two salts.[2]

Thorium Chloride, $ThCl_4$.—This is obtained by heating the oxide mixed with carbon in a current of chlorine. It has the specific gravity 4·59, melts at 820° (Moissan and Martinsen),[3] and sublimes in white shining tablets, its vapour density being 12·42, corresponding to the above formula. It deliquesces on exposure to the air, and its solution may be obtained by dissolving the hydroxide in hydrochloric acid. The strongly concentrated solution solidifies to a fibrous crystalline mass which on heating emits hydrogen chloride. It forms hydrates with 7, 8, and 9 molecules of water, whilst a number of oxy- and hydroxy-chlorides have been described.[4] It forms with the chlorides of the alkali metals easily soluble double salts, as $KCl,2ThCl_4,18H_2O$.

Thorium forms a bromide and an iodide which are similar in their behaviour to the chloride.

Thorium Sulphide, ThS_2.—The metal burns in sulphur vapour with great brilliancy, forming a yellow powder which exhibits a metallic lustre under the burnisher, and has probably the above composition (Berzelius). It has been prepared pure by passing dried hydrogen sulphide over thorium sulphate at a low red heat. It is a yellow powder which inflames spontaneously in the air.[5] When carbon disulphide vapour is passed over thorium dioxide heated to redness it yields the *oxysulphide*, ThOS, as a light brown substance.[6]

[1] Chauvenet, *Compt. rend.*, 1908, **146**, 489.

[2] Rosenheim, Samter and Davidsohn, *Zeit. anorg. Chem.*, 1903, **35**, 424.

[3] *Compt. rend.*, 1905, **140**, 1510.

[4] Rosenheim and Schilling, *Ber.*, 1900, **33**, 977; Rosenheim, Samter and Davidsohn, *Zeit. anorg. Chem.*, 1903, **35**, 424; Krüss, *ibid.*, 1897, **14**, 361.

[5] Hauser, *Zeit. anorg. Chem.*, 1907, **53**, 74. Compare also Duboni, *Compt. rend.*, 1908, **146**, 815.

[6] Krüss, *Zeit. anorg. Chem.*, 1894, **6**, 49.

Thorium Sulphate, $Th(SO_4)_2$, is obtained by dissolving the oxide in hot concentrated sulphuric acid, or by rubbing up powdered thorite or orangite to a paste with sulphuric acid, and heating the mixture to 500° until all the excess of sulphuric acid is driven off. The mass is then treated with cold water and boiled; a crystalline precipitate remains, and this may be purified by repeated solution in cold water and reprecipitation by boiling. If the solution be allowed to evaporate at the ordinary temperature, transparent monoclinic crystals of $Th(SO_4)_2,9H_2O$ are deposited, whereas above 43° a hydrate with $4H_2O$ is formed. Several other hydrates have also been obtained.[1] Thorium sulphate forms double salts with the sulphates of the alkali metals; $Th(SO_4)_2,2K_2SO_4,2H_2O$ crystallises in regular prisms, which are easily soluble in water but do not dissolve in a solution of potassium sulphate.

Thorium and Nitrogen.—A nitride, Th_3N_4, is formed [2] when metallic thorium is heated in a current of nitrogen, whilst a nitride of the same composition is obtained by reducing the dioxide with magnesium or aluminium in an atmosphere of nitrogen.[3] The latter compound, however, differs from the former in that it is not decomposed by water.

Thorium Nitrate, $Th(NO_3)_4,12H_2O$, is a very soluble salt crystallising in large deliquescent tablets. A nitrate has also been obtained crystallising with $6H_2O$,[4] and many double salts with other nitrates are known.[5]

The *phosphate* is insoluble both in water and phosphoric acid.

Thorium Borides, ThB_4 and ThB_6, have been prepared by heating thorium dioxide with amorphous boron in the electric furnace.[6]

Thorium Carbide, ThC_2, is prepared by heating thoria with sugar charcoal in the electric furnace, and forms a crystalline mass which is only slightly affected by concentrated acids but readily dissolves in dilute acids and is decomposed by water with evolution of a mixture of methane, ethylene, acetylene, and hydrogen.[7]

[1] Roozeboom, *Zeit. physikal. Chem.*, 1890, **5**, 198.

[2] Matignon and Delépine, *Compt. rend.*, 1901, **132**, 36.

[3] Kohlschütter, *Annalen*, 1901, **317**, 158; compare Matignon and Delépine, *Ann. Chim. Phys.*, 1907, [8], **10**, 130.

[4] Fuhse, *Zeit. angew. Chem.*, 1897, **4**, 115.

[5] Meyer and Jacoby, *Zeit. anorg. Chem.*, 1901, **27**, 359.

[6] Binet du Jassonneix, *Compt. rend.*, 1905, **141**, 191.

[7] Moissan, *Compt. rend.*, 1896, **122**, 573; see also Moissan and Etard, *Ann. Chim. Phys.*, 1897, [7], **12**, 427.

Thorium Silicide, $ThSi_2$, is obtained by heating a mixture of the double fluoride of potassium and thorium, potassium silicofluoride, and powdered aluminium at 1200°, or by heating silicon with thoria in the electric furnace.[1] It forms tetragonal plates of specific gravity 7·96.

Detection and Estimation of Thorium.

388 The compounds of this metal give no characteristic blowpipe or flame reaction. The alkalis and ammonium sulphide precipitate from its solutions the hydroxide insoluble in excess, and the carbonates give rise to a precipitate of a basic carbonate, which dissolves in an excess of the reagent. Ammonia produces no precipitate in this solution as it does in the corresponding one containing zirconium. Another characteristic property of thorium is its reaction with potassium sulphate, and especially the fact that the thiosulphate is thrown down from thorium solutions on addition of potassium thiosulphate, a reaction by which this metal may be separated from the metals of the cerium group. In order to separate it from titanium, columbium, and tantalum, ammonium oxalate is added to the solution, when the thorium alone is precipitated; if, however, an excess of ammonium oxalate be used the thorium oxalate dissolves. Thorium can be separated from zirconium by throwing down both metals as oxalates by ammonium oxalate, and then adding an excess of oxalic acid when the zirconium oxalate dissolves completely, leaving behind the oxalate of thorium. Thorium is estimated as the oxide, obtained by igniting the precipitated hydroxide.

The Atomic Weight of thorium was determined by several chemists without concordant results. Thus Berzelius [2] found 235·5, and Delafontaine [3] 229·7 as the mean of several well-agreeing analyses of the sulphate. Cleve, by the same method, obtained the number 232·6, whilst analyses of the oxalate yielded him the number 232·2. On the other hand, Krüss and Nilson, by analysing the carefully purified sulphate, obtained as a mean of several consistent experiments,[4] the number 232·4, which is now (1913) adopted.

[1] Hönigschmid, *Compt. rend.*, 1906, **142**, 280.
[2] *Pogg. Ann.*, 1829, **16**, 385. [3] *Arch. Sci. phys. nat.*, 1863, **18**, 343.
[4] *Ber.*, 1887, **20**, 1665. Compare Meyer and Gumperz, *Ber.*, 1905, **38**, 817.

THE GERMANIUM GROUP.

GERMANIUM. Ge = 72·5.

389 This element was discovered in 1886 by Winkler in the course of an investigation of a new silver mineral found at Freiberg in 1885, and termed argyrodite, $GeS_2,4Ag_2S$. The preliminary investigation led him to suppose that the new element would occupy the vacant place between antimony and bismuth in the periodic classification,[1] but further examination showed that the new element was tetravalent, and identical with the ekasilicon predicted by Mendeléeff. The close agreement between the predicted properties of the element and its compounds, and those actually observed by Winkler, has already been mentioned (p. 68).

Germanium is an extremely rare element, having only been found in the above mineral and also to the extent of 0·1 per cent. in euxenite.[2] It is as a rule tetravalent, and its compounds for the most part closely resemble those of silicon and the other tetravalent elements.

Metallic germanium is best obtained by the reduction of germanium dioxide with carbon at a full red heat. The semi-crystalline regulus is washed with water to remove carbon, and fused with a little borax. It is thus obtained as a greyish-white, brittle, lustrous metal, which frequently crystallises in octahedra, has a specific gravity of 5·469, melts about 960°, and is not markedly volatile at 1350°. It oxidises at a high temperature, is insoluble in hydrochloric acid, but dissolves in aqua regia, and is converted by nitric acid into the dioxide. It combines directly with the halogens.

[1] *Ber.*, 1886, **19**, 210. [2] Krüss, *Ber.*, 1888, **21**, 131.

COMPOUNDS OF GERMANIUM.

390 Germanium forms two oxides, germanium dioxide, GeO_2, and germanium monoxide, GeO.

Germanium Dioxide, GeO_2, is the most important of these and is obtained from argyrodite as follows: the powdered mineral is mixed with nitre and potassium carbonate, and the mixture is introduced in small quantities at a time into a red-hot Hessian crucible. On cooling, two layers are obtained, and the upper one, which contains all the germanium, is powdered, extracted with water, the solution treated with sulphuric acid and evaporated to dryness. The acid residue dissolves in cold water, but almost all the germanium is deposited as oxide on standing; the remainder is precipitated as sulphide, and is converted into oxide by heating with nitric acid. To purify the crude oxide it is dissolved in hydrofluoric acid, and potassium fluoride added; potassium germanofluoride separates out, and is converted into a soluble thio-salt by fusion with potassium carbonate and sulphur, this being decomposed by sulphuric acid, and the germanium precipitated as sulphide with sulphuretted hydrogen. The sulphide, when mixed with a little sulphuric acid and heated, yields a mixture of sulphide and oxide, which is converted into the pure oxide by roasting and treating with nitric acid. Thus prepared it forms a dense white powder, which is somewhat soluble in water, 1 part of the dioxide dissolving in 247·1 parts of water at 20°, and in 95·3 parts at 100°; the solution on evaporation deposits microscopic rhombic crystals. Germanium dioxide has acid properties, but also dissolves in acids; it is readily reduced by carbon, sodium and magnesium.

No germanium hydroxide of definite composition has been prepared, but a colloidal hydrate is obtained by decomposing an alkaline solution of the dioxide with carbon dioxide.

Germanous Oxide, GeO, is obtained by heating the dioxide with a small quantity of magnesium, or by heating the hydroxide; it forms a greyish-black powder. The corresponding *hydroxide* $Ge(OH)_2$, is obtained as a yellow or yellowish-red precipitate by the action of alkalis on germanium dichloride or germanium chloroform, and is soluble in excess of the alkali. Hantzsch[1] has shown that when this excess is neutralised with hydro-

[1] *Zeit. anorg. Chem.*, 1902, **30**, 289.

chloric acid, some germanous hydroxide remains in solution. From the conductivity of this solution and also of the alkaline solution, and from measurements of the rate at which the alkaline solution saponifies ethyl acetate, he concludes that germanous hydroxide in aqueous solution is a weak monobasic acid of the same type as formic acid, and has the constitution HGeO.OH, whilst in alkaline solution the salt HGeO.ONa is present. In aqueous solution part of the hydroxide is also present in the form $Ge(OH)_2$.

Germanium Hydride, GeH_4, is formed when the tetrachloride is reduced with sodium amalgam. The hydrogen evolved burns with a bluish-red flame which deposits a mirror on a cold porcelain surface. A mirror may also be obtained from the tetrachloride in the same way as in Marsh's arsenic test, and on heating in air is converted into the white dioxide, whilst the hydrogen evolved as above gives a black precipitate with silver nitrate, and this on treatment with nitric acid gives germanium dioxide.[1]

Germanium Tetrafluoride, GeF_4, has not been prepared in the anhydrous state, but large crystals containing three molecules of water are obtained by concentrating a solution of the dioxide in hydrofluoric acid. It combines with hydrofluoric acid to form *germanofluoric acid*, which has not been prepared pure; its *potassium* salt, K_2GeF_6, is prepared by adding potassium fluoride to a solution of the dioxide in hydrofluoric acid, and forms hexagonal crystals, isomorphous with those of ammonium silicofluoride, which are sparingly soluble in cold, but readily in hot water.

Germanium Tetrachloride, $GeCl_4$, is obtained by the direct union of germanium and chlorine, but is best prepared by heating the metal or the sulphide with mercuric chloride; it is a thin, colourless liquid, which fumes in the air, has a specific gravity of 1·887 at 18°, and boils at 86°. It is slowly decomposed by water with formation of hydrated germanium dioxide.

Germanium Chloroform, $GeHCl_3$.—When germanium is heated in a current of hydrogen chloride it becomes red-hot, and a distillate is obtained which, after exposure to the air, separates into two layers. The heavier of these consists of germanium chloroform, which is a colourless fuming liquid, boiling at 75°. The lighter layer is *germanium oxychloride*, $GeOCl_2$, which is also a colourless liquid, but is less mobile than germanium chloroform, does not fume in the air, and boils considerably

[1] Voegelen, *Zeit. anorg. Chem.*, 1902, **30**, 325.

above 100°. *Germanium dichloride*, $GeCl_2$, is also known ; it is a colourless, fuming liquid.

Germanium Disulphide, GeS_2.—This compound, which is the most characteristic of the germanium derivatives, is prepared by the action of sulphuretted hydrogen on a solution of germanium dioxide, or by the addition of an excess of a mineral acid to a solution of an alkali thiogermanate, sulphuretted hydrogen being passed through the solution to complete the precipitation. It is a white powder, which is only wetted with difficulty by water, in which, however, it is appreciably soluble, 1 part dissolving in 221·9 parts of cold water; it also readily dissolves in ammonium sulphide. The thiogermanates are obtained by fusing germanium derivatives with an alkali carbonate and sulphur.[1]

Germanium Monosulphide, GeS, is obtained by carefully heating the disulphide in a current of hydrogen, and forms thin plates having a greyish-black colour and an almost metallic lustre. The reduction easily proceeds further, with formation of metallic germanium. When dissolved in alkalis and reprecipitated by acid, it forms brown, amorphous flakes which dissolve in hot concentrated hydrochloric acid with evolution of sulphuretted hydrogen.[2]

Detection and Estimation of Germanium.

391 Germanium salts impart no colour to the Bunsen flame, but the spark spectrum exhibits a number of bright lines, especially in the blue and violet regions, the following among others having been measured: 6021, 5893, 5131, 4814, 4743, 4685, 4261, 4179. It is most readily recognised by the formation of the white sulphide, soluble in excess of ammonium sulphide, and this compound is also the most suitable yet known for its gravimetric estimation. The atomic weight of germanium was determined by Winkler by the analysis of pure germanium chloride, the average value found being 72·5.

TIN (Stannum). Sn = 119·0.

392 This metal was known in early times. It is very uncertain whether the word "bedil" in the Old Testament, which is

[1] *J. pr. Chem.*, 1886, [2], **34**, 182 ; 1887, [2], **36**, 177.
[2] *Ber.*, 1888, **21**, 131.

translated by the Greek word *κασσίτερος*, and by the Latin *stannum*, was originally used to designate tin. It is likewise doubtful whether the metal which the Phœnicians are said to have brought from the Cassiterides, whose exact locality was unknown to Herodotus, was really tin. Possibly the Greek word is connected with the Arabic "kasdir," which signifies tin. It is, however, certain that at the beginning of our era the word was used to specify tin, for Pliny states that *cassiteron* and *plumbum candidum* are the same, and he adds that it is more expensive than *plumbum nigrum* (lead); he, moreover, states that it serves for soldering the latter metal, and that it is obtained from the Cassiterides in the Atlantic Ocean. That the Cassiterides really were the British Islands appears more than probable, for after Cæsar's conquest tin was carried from the Cornish mines through Gaul, by way of Marseilles to Italy;[1] and Diodorus Siculus mentions that the inhabitants carry the tin to a certain island called Iktis, lying on the coast of Britain. "During low water the intermediate space is left dry, and they then carry over abundance of tin to this place in their carts." There can be little doubt that the Iktis of Diodorus is St. Michael's Mount, in Mount's Bay, in Cornwall; for up to the present day a causeway exists, flooded at high water, but dry at low water, across which the inhabitants are in the habit of carrying goods to and from the mainland. The names by which Pliny designates tin and lead seem, however, to show that he did not consider these as distinct metals, but rather as varieties of one metal, and he adds, "Sequitur naturæ plumbi cujus duo genera, nigrum atque candidum." The word *stannum*, which at a later period became the general designation for tin, also occurs in Pliny's works, though it appears certain that by this word he did not signify tin, but rather any mixture of metals which contains lead. In the works of the Latin Geber the most important properties of tin are mentioned, such as the peculiar crackling sound which the metal emits when bent, as well as the fact that it forms brittle alloys. Tin was termed Hermes by the early Greek alchemists, but about A.D. 500 it received the name of Zeus or Jupiter, and to it the sign ♃ was given; owing to the above-mentioned property of forming brittle alloys it was, however, sometimes termed *diabolus metallorum*.

Tin has been found in small quantities in Siberia, Guiana, and Bolivia in the native state, together with metallic gold, though

[1] G. Smith, *The Cassiterides*. London, 1863.

the metallic tin from the last-named locality may, according to Forbes, possibly have been an artificial product. It has also been found in small tablets in bismuthite from Mexico.

The chief ore of tin is cassiterite, or tinstone, a more or less pure form of the dioxide, SnO_2. Less frequently it is found as tin pyrites, $Cu_4SnS_4,(Fe,Zn)_2SnS_4$, and occasionally as silicate. It also occurs in small quantity in certain epidotes, as well as in columbites, tantalites, and other similar minerals. Various mineral waters likewise contain traces of tin, and this metal has also been detected in certain meteoric masses.

393 *The Metallurgy of Tin.*[1]—Almost all commercial tin is obtained from tinstone, which is found in veins traversing the older crystalline and schistose rocks, and also as *stream tin* in water-worn nodules amongst the detritus of the same rocks. Tin ore is not, however, very widely distributed, only occurring in large masses in a few localities. The oldest and best known tin mines from which tin has continuously been obtained, probably from the time of the Phœnicians up to the present, are those of Cornwall. The ore there occurs in the granite and in the metamorphic schistose rock, and is found especially rich in the killas, a metamorphic clay slate, and in the line of junction of this with granite. It is found in veins or lodes, in beds or flats, and in ramifications of small veins or "stock werke," and these tin veins usually run in Cornwall in an easterly or westerly direction. The following minerals are frequently found together with tinstone: wolfram, apatite, topaz, mica, tourmaline, arsenical pyrites, &c.

Tin mines exist, though on a much smaller scale than in Cornwall, in other parts of Europe, as in Saxony, Bohemia, Russia, Sweden, France, and in the Spanish province of Galicia. Very large deposits of tin ores are, however, found in other quarters of the globe. Thus, for instance, in the Island of Banca, and on the Malay Peninsula, large quantities of tin ore are found, chiefly in the form of stream tin, though it likewise occurs in lodes in granite rocks. This source of tin was discovered at the beginning of the eighteenth century, and at a later time very rich mines, which are now worked, were discovered in the neighbouring Islands of Bilitong, Sumatra, and Carimon.

Tin has also been found in Bolivia, Peru, United States,

[1] See also *Metallurgy of Tin.* Henry Louis. McGraw-Hill Book Company, 1911.

New South Wales, Queensland, Tasmania, Burma, Siam, China, Northern Nigeria, South Africa, &c.

Tin ores may be smelted in shaft furnaces or in reverberatory furnaces, but as the ores obtained are generally very poor, containing only from 1 to 2 per cent. of tin, preliminary operations of dressing or concentration are always necessary, and as considerable losses are experienced in these operations, much attention is being given to the direct treatment of tin-bearing material, and many suggestions have been put forward. These, however, are not in a sufficiently advanced state to be considered in detail.

The process adopted in Cornwall for the reduction of the metal is a simple one. The ore, which consists not only of Cornish stone, but likewise of Australian and Peruvian ore, after being stamped, is washed to free it as much as possible from gangue, and is then roasted in calcining furnaces for the purpose of driving off the sulphur and arsenic contained in the arsenical and ordinary pyrites, if these be present.

The vapours from these revolving calcining furnaces are led into chambers in which the arsenious oxide condenses. The construction of an Oxland and Hocking's revolving calciner is shown in Fig. 178. This consists of a long cylinder lined with firebrick and placed in an inclined position. The fire (H) is placed at the lower end (A), whilst the upper end is in connection with chambers in which the arsenious oxide condenses. The ore is dried on the top of these chambers, which are made of iron plate, and then brought by means of the hopper (h) into the cylinder, the roasted ore falling down into the space (F). This then undergoes a second washing in order to remove the ferric oxide and other oxidised materials, and is again roasted for the purpose of volatilising the last traces of arsenic and sulphur. After these operations the roasted ore is found to contain from 60 to 70 per cent. of tin. It sometimes happens that the tin ore is mixed with more or less wolfram, $(Fe,Mn)WO_4$, and as this mineral possesses a high specific gravity it cannot be removed from the tin ore by washing. In order to remove this impurity, the presence of which in the smelting operations would prove injurious to the quality of the tin obtained, the ore is passed through some form of magnetic separator which extracts the wolfram and allows the tinstone to pass on. The prepared tin ore, or *black tin*, is then mixed with one-fifth part its weight of anthracite and the mixture sprinkled with

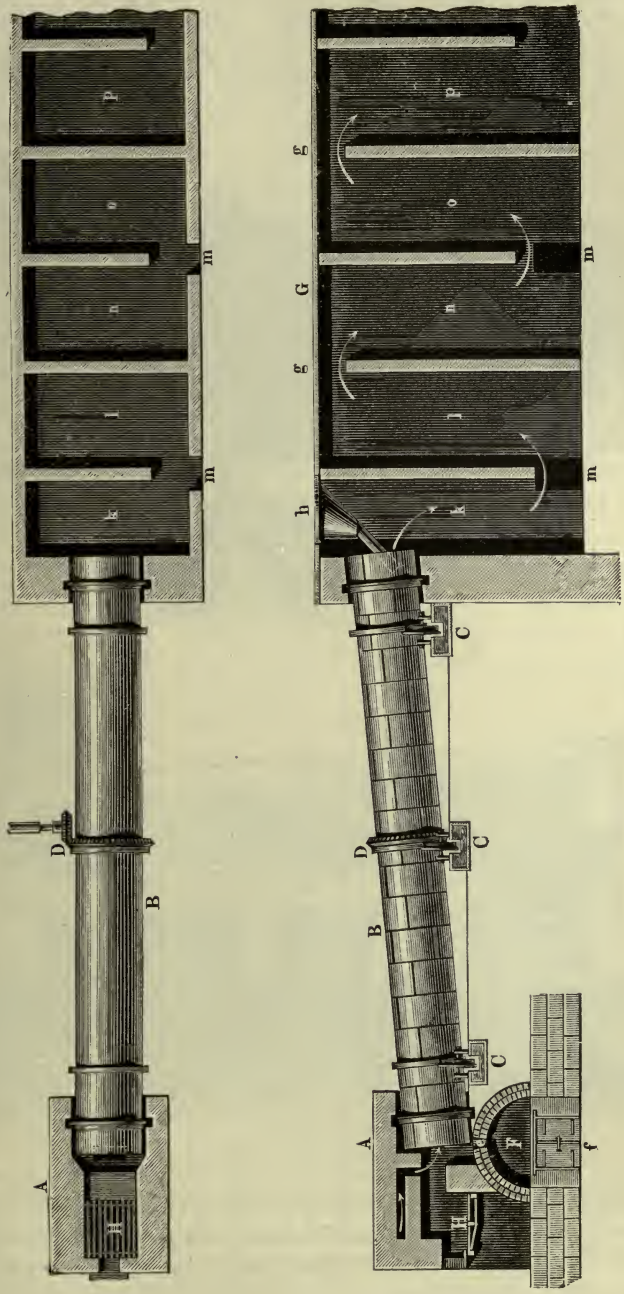


FIG. 178.

some water in order to prevent the finely divided ore from being blown by the draught into the flues. The construction of the reverberatory furnace is shown in Figs. 179 and 180: the charge is introduced by the door (B) on to the hearth

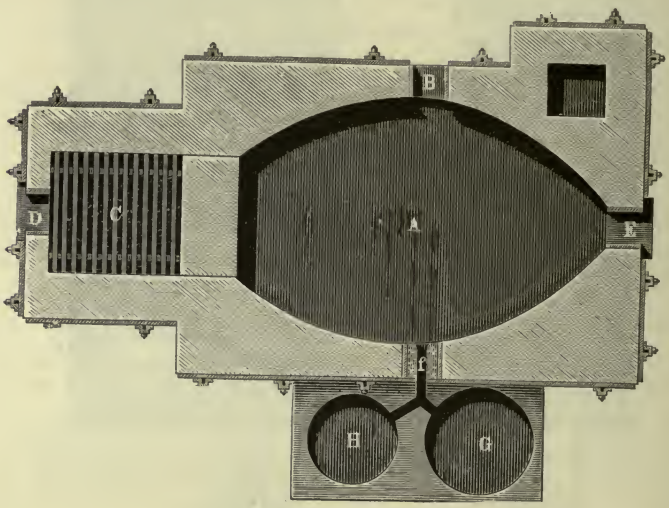


FIG. 179.

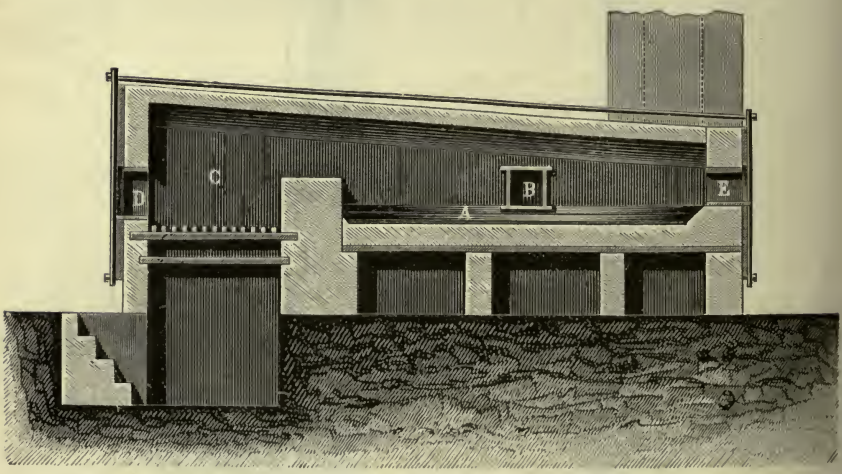


FIG. 180.

(A), and then worked through the door (E). The temperature of the furnace is gradually raised for five hours, the charge then repeatedly stirred, and at the expiration of six hours the reduced metal is tapped and allowed to run from the lower part of the

hearth through the hole (f) into the vessel (G). The impure tin thus obtained is then cast into moulds, and these are refined by the process of *liquation*. This is effected by placing the ingots in another similar reverberatory furnace which is gradually heated, so that the pure, more easily fusible tin first melts and runs into a cast-iron vessel (H) placed below, whilst the less fusible alloy of tin with iron and arsenic remains on the hearth. A fire is placed under the vessel (H) in order to keep the metal liquid, and this is then stirred up with a pole of green dense wood. The length of this operation depends upon the quality of the metal which it is desired to obtain, and may last from one to several hours. The dross which separates during the process of refining, and the "hard-head," or residue which remains on the hearth, both of which contain large quantities of tin, are afterwards worked up. In order to prepare *grain tin* the tin is heated until the metal becomes brittle and crystalline; it is then broken up by a hammer, or allowed to fall from a considerable height.

The slags formed during the smelting operations generally contain sufficient tin to be worth extraction. This tin may exist as prills of metal or in chemical combination. The metallic portion is often separated by crushing and washing, or by allowing the slag to stand in a molten condition for some hours, when the metallic tin settles to the bottom. Slags containing tin in the combined condition are re-smelted with dross and other residues and strong bases at high temperatures in shaft or reverberatory furnaces.

394 *Separation of Tin from Tin Scrap, &c.*—Tin is separated from tin scrap and tin can waste by means of dry chlorine gas. The tin waste is washed in an alkaline bath to remove grease, rinsed in water, then heated in a furnace to remove solder, and then treated in iron cylinders with chlorine, the cylinders being kept cool.[1] The tin chloride thus formed is put on the market, and the steel scrap, which contains less than 0·1 per cent. tin, is hydraulically pressed into briquettes, and smelted in open-hearth furnaces.

The electrolytic process formerly used, in which sodium hydrate was the electrolyte, proved expensive, as it required highly paid labour, expensive electric current, and gave as a product a tin mud of inferior quality, which required further smelting treatment to convert it into marketable tin.

[1] *Öst. Zeit. f. Berg. u. Hütt-Wesen*, 1909, **57**, 103.

The total amount of tin produced in 1911 was about 104,090 tons.[1]

395 *Properties and Uses of Tin.*—Tin is a white, brightly lustrous metal, which melts at 232° (Heycock and Neville), volatilises between 1450° and 1600° (Carnelley and Williams), and has a specific gravity at 13° of 7·293 (Matthiessen). It is harder than lead, but softer than gold. It exhibits a fibrous fracture, and when bent emits a peculiar crackling sound caused by the friction of the crystalline particles. Tin can be easily rolled or hammered out to foil, and at a temperature of 100° it may be drawn into wire, which, however, possesses but slight tenacity; at 200° it becomes so brittle that it may be powdered. A sample of Banca tin which was exposed at St. Petersburg to a very low temperature during the winter of 1867–8, fell to granular, crystalline pieces or to a coarse powder. This alteration is due to the fact that tin, like sulphur, exists in more than one form, dependent upon the temperature, the stable form below 18° being the grey powder or "grey tin." At ordinary temperatures common white tin is in a metastable condition, but the change to the stable grey tin takes place with extreme slowness. The rate of change may, however, be accelerated by lowering the temperature, the maximum velocity being reached at – 50°. This alteration was known to Aristotle, who speaks of tin as "melting" when kept at low temperatures.[2] Between 18° and 170° the stable form of tin is tetragonal, whilst above this temperature it is rhombic.[3] If zinc be brought into a solution of tin chloride the metal separates out in the form of fine crystalline dendrites, and this deposit, known as the tin-tree (Arbor Jovis), was first prepared by Ilsemann in 1786. When tin is melted and then allowed partially to solidify, the liquid portion being poured off, needle-shaped prismatic or tabular crystals of the metal remain behind. Another mode of obtaining crystalline tin is to decompose tin chloride by a weak electric current, when the metal is deposited in tetragonal prisms and pyramids. Fine crystals of tin can also be obtained when water containing zinc dust in suspension is gradually added to a solution of tin chloride.

[1] *Mineral Industry*, 1911, **20**, 704.

[2] Cohen and van Eyk, *Zeit. physikal. Chem.*, 1899, **30**, 601; Hasslinger, *Monatsh.*, 1908, **29**, 787; Cohen, *Zeit. physikal. Chem.*, 1908, **63**, 625; 1909, **68**, 214.

[3] Findlay, *The Phase Rule*, p. 39 (Longmans, 1904); Cohen and Goldschmidt, *Zeit. anorg. Chem.*, 1904, **50**, 225.

Metallic tin remains bright in dry or moist air at the ordinary temperature, but when melted gradually oxidises, forming a greyish-white skin on the surface, which consists of a mixture of tin and stannous oxide and is gradually oxidised to the dioxide. It is dissolved by dilute, and more rapidly by concentrated hydrochloric acid, with evolution of hydrogen and formation of stannous chloride; it dissolves also in aqua regia and in hot concentrated sulphuric acid, and is converted by somewhat diluted nitric acid into metastannic acid. It dissolves also in aqueous solutions of the alkalis, with formation of salts of metastannic acid and evolution of hydrogen.

Tin is used for a large number of purposes, for the preparation of vessels for household and technical use, for the manufacture of tinfoil, for tinning copper and iron, and especially for preparing the alloys of tin. Tinned copper vessels were employed by the ancients, for we find them described by Pliny; and the same author also mentions as a well-known fact that in the process of tinning, the weight of copper articles increases but slightly, and he adds that the substance termed stannum is employed for this purpose.

Copper- and brass-ware can readily be tinned by dipping the vessel into the molten metal. In order to cover the interior of a vessel with a coating of tin, it is heated and some molten tin poured in, which is then well divided over the surface by rubbing with rags. In order to prevent the oxidation of the metal a small quantity of resin or sal-ammoniac is added. Agricola was the first to mention the process of tinning iron. It appears, however, that at that time it was only slightly employed. The process is usually supposed to have been discovered in Bohemia in 1620, coming into use in England and France about 100 years later. For the purpose of preparing the common tin plate, the iron plate is dipped into hydrochloric acid or dilute sulphuric acid, then rubbed over with sand and water, and lastly dipped into a bath of hot fat, in order to dry and warm it. From this it is brought into a vessel filled with melted tin covered with a film of oil, an alloy of tin and iron being thus formed. This is covered with a film of pure tin by dipping it into a second bath of the metal, and the sheets are lastly dipped into heated tallow in order to remove the excess of tin.

Alloys of Tin.

396 Several of these alloys are largely employed in the arts. Tin and lead may be mixed in any proportion, and the alloys are harder and tougher, but more readily fusible than either of the two metals. For this reason they are employed as solders. The following table gives the composition of some of the different lead and tin alloys:

	Common Pewter.	Solder.		
		Fine.	Common.	Coarse.
Tin . . .	4	2	1	1
Lead . . .	1	1	1	2

In practice, a certain amount of antimony is often used to replace some of the tin in these alloys.[1]

Bronze is the name given to any alloy consisting chiefly of copper and tin, although other elements are frequently added to impart particular properties.

The alloys corresponding in composition to the formulæ $SnCu_3$ and $SnCu_4$ are definite chemical compounds, and are the only ones of the series which remain homogeneous after melting, a certain amount of liquation taking place in all the others. The hardness of these alloys increases as the proportion of copper is increased from pure tin to 35 per cent. of copper; from 35 per cent. to 73 per cent. of copper the alloys are extremely brittle, and beyond 73 per cent. of copper, the hardness diminishes as the copper is increased. The effect of heat on some of the copper-tin alloys is remarkable, for whilst steel is hardened by quenching in water, these alloys are hardened by slow cooling and when quenched in water they lose their brittleness and become malleable.

Gun-metal usually contains 9 parts of copper to 1 of tin, and has a yellow colour. This alloy also serves for the preparation of bronze medals.

Speculum-metal is composed of 1 part of tin to 2 parts of copper, melted together, with, frequently, addition of a small quantity of arsenic. It possesses a steel-grey colour, is very brittle, and takes a very high polish.

Bell-metal possesses a varying composition. It generally consists of from 4 to 5 parts of copper to 1 of tin. It has a

[1] See Bannister and Tabor, *Journ. Inst. Metals*, 1909, **2**, 58.

yellowish-grey colour, and readily melts to form a thin liquid. It has a finely granular structure, is hard, brittle, and very sonorous. The Chinese gongs and tom-toms are cast at a very high temperature, and then quickly brought under the hammer, in consequence of which treatment the alloy becomes very dense.

The annexed table (p. 852) gives the composition of some of the alloys described above.

Phosphor-bronze.—The addition of phosphorus to bronze imparts to it a character of greater hardness, elasticity, and toughness. This material is obtained by melting copper with tin phosphide, sometimes with a small addition of lead. It contains from 0·25 to 2·5 per cent. of phosphorus, and from 5 to 15 per cent. of tin, and is largely used, especially that containing from 7 to 8 per cent. of tin, for portions of machinery for which hardness and toughness are important properties. The alloy containing more tin has been employed for bell-metal. Its valuable properties are connected with the fact that copper forms a homogeneous alloy with tin phosphide, the presence of phosphorus preventing the oxides from dissolving and thus impairing the qualities of the metal.

Tin Amalgam.—Tin readily combines with mercury with lowering of temperature. The amalgam may be formed more quickly when mercury is poured into molten tin, and, according to the quantity of mercury added, the amalgam is either liquid, or forms a granular or crystalline mass. When mercury is made the negative pole in a solution of tin dichloride, fine crystals of the amalgam are obtained containing from 44 to 51 per cent. of tin (Joule). Tin amalgam is largely used for silvering mirrors. For this purpose tin foil, which usually contains from 1 to 2 per cent. of copper and a small quantity of lead, is spread out on a perfectly even horizontal slate table. This is then covered with a film of mercury from about 2 to 3 mm. in thickness, and the carefully cleaned sheet of plate glass floated on to its surface, the excess of mercury being pushed forward and the formation of bubbles of air thus guarded against. The glass is then gradually weighted evenly throughout its surface in order to remove the excess of mercury. After the lapse of some time the weights are removed and the plate gradually inclined in order that the excess of liquid amalgam may flow away.

It is not certain when this process for manufacturing mirrors was first employed, inasmuch as, during the middle ages, the

Analyses of Alloys of Tin.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Cu .	91·74	67	73·94	82	84·25	87·89	84·53	85·9	70·30	89·43	89·78	88·77	89·34	84·20
Sn .	8·26	33	21·67	17	15·64	10·58	6·82	14·1	24·53	8·17	9·16	9·25	7·50	3·05
Pb .	—	—	1·19	—	—	—	8·65	—	5·20	1·05	1·33	0·71	1·21	0·75
Fe .	—	—	0·17	1	trace	0·27	—	—	—	0·34	—	—	—	—
Zn .	—	—	—	—	—	—	—	—	—	—	0·35	1·28	1·61	11·55
Ni .	—	—	2·11	trace	—	—	—	—	—	0·19	—	—	—	—

I. English gun metal.
II. Speculum metal used in construction of Lord Rosse's large telescope.
III. Bell cast in 1670 in Darmstadt.
IV. Chinese gong.
V. Egyptian bronze coin of the reign of Ptolemy IX.
VI. Attic bronze coin.
VII. Roman bronze coin of Justinian.
VIII. Gaulish axe.
IX. Celtic arrow-head.
X. Bronze statue of sixteenth century from Augsburg.
XI. Statue of Germanicus, cast in Berlin in 1824.
XII. Thorwaldsen's Shepherd, cast in Berlin in 1825.
XIII. Statue of Bacchus in Berlin, 1830.
XIV. Statue of Lessing in Brunswick.

processes used in the preparation of mirrors were kept secret. It is, however, clear that before amalgam was used, a surface of metallic lead was employed for obtaining a mirror as early as the thirteenth century, when such mirrors were common. These were curved, and were prepared, as Beckman describes in his *History of Inventions*, from large glass globes, into the interior of which a mixture of resin, molten lead, and sulphide of antimony was introduced, the fluid mass being brought over the surface until it was all covered with a thin film. The globe was then cut into pieces, and the mirrors thus obtained were often employed as ornaments. A guild of glass-mirror makers existed at Nuremberg in the year 1373; whether they made mirrors according to the above process is doubtful, but they, as well as French workmen, sold products of their art in the Venetian market up to the year 1500. The use of amalgam for coating mirrors is first mentioned by Kunkel, who recommends for the purpose an amalgam of 2 parts of quicksilver, 1 of marcasite (bismuth), ½ part of tin, and ½ part of lead.

COMPOUNDS OF TIN.

Tin and Oxygen.

397 The fact that tin readily forms a calx was observed at an early period. Pelletier was the first, in the year 1792, to show that tin combines in two proportions with oxygen, forming two series of salts. This investigation was continued by Proust, but for a long time considerable doubt existed as to the number of the oxidation products of the metal. Berzelius in 1812 assumed that there were three oxides, SnO, Sn_2O_3, and SnO_2, on the grounds that when the metal is oxidised by nitric acid the highest oxide thus prepared possesses a totally different chemical character from that obtained by precipitation with alkalis from a solution of the salts of tin. The subsequent investigations of Davy, Gay-Lussac, and Berzelius himself, have proved that only the first and last of these oxides exist. A peroxide, SnO_3, has also been prepared.

Tin Monoxide or *Stannous Oxide*, SnO.—This oxide may be prepared in a variety of ways. In the first place it is obtained as an olive-coloured powder when stannous oxalate is ignited out of contact with air. Secondly, it may be prepared by adding

a solution of potassium carbonate to one of tin dichloride, when a white precipitate having the composition $Sn_2O(OH)_2$ is thrown down. This readily absorbs oxygen from the air, but if it be washed in absence of air and dried in a stream of carbon dioxide, the monoxide remains behind as a black powder. Stannous oxide is also obtained when the pure dichloride is mixed with sodium carbonate, the mass heated until it has become black, and then lixiviated. If the hydrated oxide be boiled with a dilute solution of caustic potash, the anhydrous oxide is obtained as a crystalline powder, the crystals consisting of combinations of the cube and dodecahedron. It may also be obtained in the crystalline state by digesting a nearly saturated solution of the hydrated oxide in acetic acid at a temperature of 56°.

According to Hantzsch [1] the hydroxide SnO_2H_2 is precipitated when caustic soda is added to a solution of stannous chloride in the absence of air. It dissolves in excess of the reagent, and, like germanous hydroxide, acts as a weak monobasic acid of the type of formic acid, the solution containing sodium stannite, H·SnO·ONa.

Stannous oxide readily takes fire when heated in the air, and dissolves in acids with formation of stannous salts, to which it corresponds. These are, however, more readily obtained by the action of acids upon the metal, and possess an unpleasant metallic taste, redden litmus, owing to hydrolysis, readily absorb oxygen, and serve as powerful reducing agents.

Tin Dioxide or *Stannic Oxide*, SnO_2, occurs in nature as tinstone or cassiterite, crystallising in the tetragonal system (Fig. 181), and possessing an adamantine lustre. The crystals are seldom colourless, being generally tinted brown or black from the presence of the oxides of manganese and iron. *Stream-tin* is found in water-worn nodules, and *Wood-tin* in reniform fibrous masses. When tin is heated nearly to its boiling point in the air, it burns with a luminous, white flame, and the dioxide which is thus formed in a state of fine division was formerly known as *flores jovis*. If fused in the presence of air, the surface of the metal soon becomes covered with a grey pellicle, which then passes into a grey powder known as *flores stanni*, consisting of a mixture

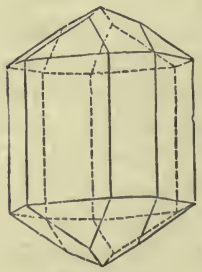


Fig. 181.

[1] *Zeit. anorg. Chem.*, 1902, **30**, 289.

of finely-divided metal with the oxide; the mixture, on continued ignition, is wholly converted into stannic oxide. The dioxide is also obtained on treating tin with nitric acid, when a violent oxidation occurs. The hydrated white powder thus formed yields the dioxide on washing and igniting. If a solution of stannic chloride be precipitated with ammonia, a gelatinous precipitate is obtained which can be completely washed only with difficulty. If, however, it be heated with a concentrated solution of an alkali sulphate, a dense precipitate is thrown down, and this can be easily washed and yields the pure dioxide on ignition. An amorphous, white or straw-coloured powder is then obtained, which is quite insoluble in water and possesses a specific gravity of 6·71. On heating it changes colour, becoming lemon-yellow and then brown, but it assumes its original tint on cooling.

The dioxide may also be obtained by the electrolysis of a solution of potassium or sodium chloride, a tin plate being used as anode, and one of platinum as cathode.[1]

By heating amorphous stannic oxide in a current of hydrogen chloride it may be obtained in microscopic crystals which have the form of cassiterite and a specific gravity of 6·72 (Deville).[2] The formation of crystalline stannic oxide has been observed in fusing the dross collected on the hearth of a gun-metal furnace, the crystals being hard, brittle, four-sided prisms.[3] Stannic oxide can be fused only at a very high temperature, according to Cusack[4] 1127°. It is not volatile, nor is it attacked by concentrated acids, with the exception of sulphuric acid.

Stannic Hydroxides.—Two isomeric stannic hydroxides are known, each of which behaves as an acid, yielding a corresponding series of salts. From analogy it would be expected that the acids would correspond to meta- and ortho-silicic and titanic acids, and have the compositions H_2SnO_3 and H_4SnO_4; as, however, both acids exist in all degrees of hydration between the limits required by these two formulæ,[5] the isomerism must be due to other causes. No satisfactory explanation of the difference in their constitution has, however, as yet been given. The two acids are distinguished as *stannic* and *metastannic acids*, or

[1] Lorenz, *Zeit. anorg. Chem*, 1896, **12**, 436.
[2] *Compt. rend.*, 1861, **53**, 161.
[3] Abel, *Journ. Chem. Soc.*, 1858, 119.
[4] *Proc. Royal Irish Acad.*, 1897, **4**, 399.
[5] See Lorenz, *Zeit. anorg. Chem.*, 1895, **9**, 376.

as *α-* and *β-stannic acids*, and each yields a series of salts from which the original acid may be again obtained by the action of stronger acids.

Stannic Acid or *α-Stannic Acid* is obtained as a white hydrated precipitate by the action of calcium carbonate on a solution of stannic chloride or bromide, or when a stannate is carefully precipitated with an acid. The well-washed precipitate, which is slightly soluble in water and has an acid reaction, has the composition H_2SnO_3 when dried over sulphuric acid, but if it be obtained by adding a concentrated solution of an alkali sulphate to a solution of stannic chloride and allowed to dry in the air it has the composition H_4SnO_4. Both of these gradually lose water on heating, the final product being tin dioxide. Stannic acid dissolves readily in dilute mineral acids as well as in the alkalis. With the latter it yields the alkali stannates which are the only ones soluble in water. The other stannates are obtained as insoluble precipitates by double decomposition.

According to Bellucci and Parravano [1] the stannates have the formula $[Sn(OH)_6]M_2$.

Potassium Stannate, K_2SnO_3, is obtained by fusing the dioxide with potash, or by dissolving the hydrated oxide in potash-lye. The solution yields on evaporation over sulphuric acid colourless, glistening, rhombic prisms of $K_2SnO_3,3H_2O$ (Marignac), which have an alkaline taste and are readily soluble in water. According to Bellucci and Parravano [2] the water in this and the corresponding sodium compound is not water of crystallisation, but these salts are derived from *hexahydroxystannic acid*, $H_2Sn(OH)_6$, and are isomorphous with the hexahydroxyplatinates. Metallic copper brought into contact with the solution becomes covered with a bright coating of tin.

Sodium Stannate, Na_2SnO_3, is prepared on a large scale and employed extensively in calico-printing under the name of *preparing salts*. It is obtained either by fusing the finely powdered or levigated tinstone with caustic soda, dissolving the mass in water to remove any ore that may be unacted upon, and evaporating the solution; or by heating tin with caustic soda and Chili saltpetre. On evaporating the solution crystals of $Na_2SnO_3,3H_2O$, or $Na_2Sn(OH)_6$, are obtained, which are more soluble in cold than in hot water. A tolerably concentrated solution of the salt which contains no caustic soda deposits on

[1] *Zeit. anorg. Chem.*, 1905, **45**, 142.
[2] *Atti R. Acad. Lincei*, 1904, [5], **13**, ii., 324; **14**, i., 457.

cooling fine prisms of the composition $Na_2SnO_3,10H_2O$, and these effloresce on exposure to air.

Metastannic Acid and the Metastannates.—In his *Reflections on the Hypothesis of Alkali and Acidum*,[1] published in 1670, Boyle remarks that aqua-fortis eats up or destroys more tin than it dissolves. On the other hand, he elsewhere[2] mentions that a solution of tin in aqua-fortis readily becomes gelatinous. Kunkel, who also studied the action of nitric acid on tin, mentions in his *Laboratorium Chymicum* that tin can only be dissolved when it is added in small quantities to an acid, and that heat must be altogether avoided, because white calx of tin is thrown down when the acid is hot. The explanation of these different statements is to be found in the facts that when the metal is treated with weak nitric acid it forms either stannous or stannic nitrate according to the degree of concentration of the acid, and that the latter salt easily decomposes with separation of a gelatinous stannic acid, whilst, on the other hand, when tin is acted upon by strong nitric acid it is violently attacked with evolution of heat and formation of an insoluble white powder consisting of metastannic acid. Metastannic acid reddens litmus, and when dried in the air contains about 20 per cent. of water, which it gradually loses when heated or when dried in a vacuum, but it is doubtful whether any definite hydrate is formed during the process.[3]

Metastannic acid is distinguished from ordinary stannic acid, inasmuch as it is altogether insoluble in nitric acid, and swells up but does not dissolve in strong sulphuric acid, forming a compound with it which is decomposed by water. When warmed with concentrated hydrochloric acid it combines with it to form a hydrochloride of metastannic acid, which is insoluble in hydrochloric acid but soluble in water, and which gelatinises on boiling, even in very dilute solution.

The salts of metastannic acid are formed by the action of the alkalis on metastannic acid or on its compound with hydrochloric acid. They all possess a very complicated composition and crystallise with difficulty. The sodium salt has been most exactly examined.

Sodium Metastannate, $Na_2Sn_5O_{11},4H_2O$, or $H_8Na_2Sn_5O_{15}$.—This is a slightly soluble, granular, crystalline powder obtained

[1] Boyle, *Op.* 4, 284.

[2] "Experiments and Considerations Concerning Colours."

[3] Compare *Compt. rend.*, 1897, 125, 464.

by the action of cold caustic soda solution on metastannic acid. If a hydrochloric acid solution of metastannic acid be precipitated with caustic soda, hard gum-like masses of a compound $Na_2Sn_9O_{19},8H_2O$ are obtained.

When solutions of stannic acid in hydrochloric acid and hydrobromic acid (which are identical with the solutions obtained by the action of water on stannic chloride and bromide) are allowed to stand, the stannic acid slowly undergoes conversion into metastannic acid, which usually separates out as an opalescent precipitate. This change takes place much more rapidly with the hydrobromic than with the hydrochloric acid solution and may in both cases be followed quantitatively by suitable means.[1] It would therefore appear that the constitution of metastannic acid is more complex than that of stannic acid, and this is confirmed by the fact that many of the metastannates have an even more complicated composition than those mentioned above.

Colloidal or *Soluble Stannic Acid* was obtained by Graham[2] by the dialysis of a mixture of tin tetrachloride and alkali, or of sodium stannate and hydrochloric acid, the gelatinous mass which is first formed gradually dissolving. The liquid is converted on heating into colloidal metastannic acid. Traces of hydrochloric acid or of a salt bring about gelatinisation in both solutions.

Tin Peroxide, SnO_3.—This oxide is known only in the hydrated condition, and is prepared by the addition of barium peroxide to a solution of stannous chloride containing hydrochloric acid. The barium chloride is removed by dialysis, and the colloidal solution is evaporated. A white mass having the formula $H_2Sn_2O_7$ or $2SnO_3,H_2O$ remains behind.[3]

When stannic hydroxide is heated with hydrogen peroxide at 70°, and the mixture is desiccated, a *perstannic acid,* $HSnO_4,2H_2O$, is obtained, and this on heating at 100° yields the acid $H_2Sn_2O_7,3H_2O$. Potassium and sodium stannates when similarly treated form salts corresponding to these acids.[4]

When concentrated alkali stannate solutions are electrolysed at low temperatures and with low current densities, perstannates are formed, owing to anodic oxidation.[5]

[1] Lorenz, *Zeit. anorg. Chem.*, 1895, **9**, 376.
[2] *Phil. Trans.*, 1861, **151**, 213.
[3] Spring, *Bull. Soc. chim.*, 1889, [3], **1**, 180.
[4] Tanatar, *Ber.*, 1905, **38**, 1184.
[5] Coppadoro, *Gazz.*, 1908, **38**, i., 489.

Stannous Compounds.

398 *Tin Difluoride* or *Stannous Fluoride*, SnF_2, is obtained by dissolving the hydrated monoxide in hydrofluoric acid. On evaporation in absence of air this compound is obtained in the form of small, white, monoclinic tablets.

Tin Dichloride or *Stannous Chloride*, $SnCl_2$, is obtained on the large scale by dissolving tin in hydrochloric acid. On evaporating the solution and cooling, crystals of hydrated stannous chloride, $SnCl_2,2H_2O$, known in commerce as *Tin Salt*, separate out in transparent, monoclinic prisms which melt in their water of crystallisation at 40°, and on cooling again yield a crystalline mass. They have a specific gravity of 2·71, and dissolve at the ordinary temperature in 0·37 part of water. When more strongly heated they partially decompose with evolution of hydrogen chloride, but when dried in a vacuum over sulphuric acid they lose their water. The anhydrous salt, which may also be obtained by heating tin in hydrogen chloride, or with the requisite amount of corrosive sublimate, is a transparent mass having a fatty lustre and conchoidal fracture. It fuses at 250° to form an oily liquid which boils at 606°. Its vapour at low temperatures has a density always less than that required by the formula Sn_2Cl_4, but at a high temperature the value becomes constant, agreeing with $SnCl_2$,[1] whilst the freezing point of urethane is lowered by dissolving stannous chloride in it by an amount corresponding to the formula $SnCl_2$.[2] The hydrated salt dissolves in a small quantity of water with lowering of temperature, forming a clear liquid which, when diluted with much water, becomes turbid, a basic chloride, $2Sn(OH)Cl,H_2O$, being precipitated; this again dissolves on the addition of acids. The same precipitate is formed when the clear solution is exposed to the action of the air:

$$6SnCl_2 + 2H_2O + O_2 = 2SnCl_4 + 4Sn(OH)Cl.$$

Stannous chloride is soluble in alcohol and in ether.[3] It combines with ammonia to form compounds which vary in composition according to the temperature of reaction.[4] When cooled in a freezing mixture, a yellow compound,

[1] Biltz and V. Meyer, *Ber.*, 1888, **21**, 22.
[2] Castoro, *Gazz.*, 1898, **28**, ii., 317.
[3] de Jong, *Zeit. anorg. Chem.*, 1902, **41**, 596.
[4] Sofianopoulos, *Compt. rend.*, 1911, **152**, 865.

$SnCl_2,2NH_3$, is formed, which blackens on exposure to light, and is decomposed by moisture into stannous oxide and ammonium chloride. At ordinary temperatures a mixture of $SnCl_2,2NH_3$ and $SnCl_2,NH_3$ results, whilst at 100° $SnCl_2,NH_3$ only is formed. At 120—300° the compound $3SnCl_2,2NH_3$ is formed as a brownish-red, crystalline mass, which is the most stable of the three compounds.

Tin Dibromide or *Stannous Bromide*, $SnBr_2$, is obtained when tin is heated in hydrogen bromide or distilled with mercuric bromide. It forms a light yellow, translucent mass fusing at 215·5°, and is soluble in water. A solution of this compound is obtained by acting with hot aqueous hydrobromic acid upon metallic tin.

Tin Di-iodide or *Stannous Iodide*, SnI_2, is best obtained by adding a small excess of iodide of potassium to a warm concentrated solution of stannous chloride. It crystallises in yellowish-red needles which dissolve only slightly in water, though readily in warm solutions of the chlorides and iodides of the alkali metals, and also in dilute hydrochloric acid. It melts at 316°, solidifying to a crystalline mass which liquefies at a higher temperature. When heated in absence of air it is obtained in the form of a red, crystalline mass, yielding a scarlet powder. On treatment with dry ammonia, a yellow compound having the formula $SnI_2,2NH_3$ is formed.[1] If a saturated solution of stannous iodide in hydriodic acid be cooled to 0°, pale yellow needles of *iodostannic acid*, $HSnI_3$, are deposited. These are very unstable and readily decompose, forming stannous iodide.[2]

The fluoride, chloride, bromide, and iodide combine with the corresponding halide compounds of the alkali metals and with those of the metals of the alkaline earths to form crystalline double salts.

Tin Monosulphide or *Stannous Sulphide*, SnS, is obtained by heating together the metal and sulphur. Thin tin foil takes fire spontaneously when brought into sulphur vapour. When thus obtained it is a lead-grey, tough, crystalline mass, which melts at a higher temperature than the metal. When a solution of stannous chloride is saturated with sulphuretted hydrogen, a brown hydrated precipitate is obtained, which on drying becomes black. This is scarcely soluble in ammonium sulphide, but dissolves on the addition of sulphur, and is also soluble in

[1] Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.
[2] Young, *J. Amer. Chem. Soc.*, 1897, **19**, 851.

the polysulphides of the alkali metals, the stannous sulphide being first converted by the sulphur into stannic sulphide, which then dissolves, forming ammonium thiostannate. When the dried precipitate is added to fused stannous chloride and the melted mass treated on cooling with dilute hydrochloric acid, stannous sulphide is obtained in metallic glistening crystalline scales, having a specific gravity of 4·973. The crystalline variety may also be obtained by heating the amorphous sulphide in the electric furnace.[1] Amorphous tin sulphide dissolves readily in hot hydrochloric acid, whilst the crystallised substance dissolves less readily.

Stannous Sulphate, $SnSO_4$, is formed by dissolving the metal or the hydrated oxide in dilute sulphuric acid. On evaporation in a vacuum, microscopic granular crystals are obtained which are only a little more soluble in hot than in cold water. The solution readily deposits a basic salt.

Stannous Nitrate, $Sn(NO_3)_2$.—This salt is obtained by the action of very dilute nitric acid on the metal, ammonium nitrate being simultaneously produced:

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

Stannic Compounds.

399 *Tin Tetrafluoride* or *Stannic Fluoride*, SnF_4, is obtained as a hygroscopic, white, crystalline substance by the action of anhydrous hydrofluoric acid on stannic chloride.[2] It boils at 705°, subliming below this temperature, and has the specific gravity 4·78 at 19°. An aqueous solution of the fluoride may be obtained by dissolving the hydrated dioxide in hydrofluoric acid; the solution coagulates on boiling, and decomposes on evaporation with evolution of hydrogen fluoride. Gaseous ammonia combines with tin tetrafluoride at 43°, forming a white compound, SnF_4,NH_3, which loses very little ammonia even at 400°.[3] When the fluoride and ammonia are heated together in a sealed tube at 120—130°, $SnF_4,2NH_3$ is formed. Both these compounds are soluble in ammonia.

Liquid hydrogen sulphide decomposes the fluoride in a sealed tube, thus: $SnF_4 + 2H_2S = SnS_2 + 4HF$.

[1] Mourlot, *Compt. rend.*, 1897, **124**, 768.
[2] Ruff and Plato, *Ber.*, 1904, **37**, 673.
[3] Wolter, *Chem. Zeit.*, 1912, **36**, 165.

Chlorine compounds of phosphorus bring about an exchange of chlorine and fluorine, and metals react violently with the fluoride, liberating tin.

It combines with other fluorides, forming a characteristic series of double salts termed the *stannifluorides*, which mostly crystallise well and are isomorphous with the corresponding double fluorides of silicon, titanium, germanium, and zirconium.[1]

Potassium Stannifluoride, K_2SnF_6,H_2O, is obtained by neutralising hydrofluoric acid with potassium stannate, or by treating stannic chloride with a cold solution of potassium fluoride.[2]

It crystallises in thin nacreous tablets, or in rhombic pyramids which are much more soluble in hot than in cold water. When the solution contains an excess of hydrofluoric acid, the salt K_2SnF_6,HKF_2 is deposited in thin monoclinic prisms.

The stannifluorides of sodium, ammonium, calcium, and magnesium are also crystalline soluble salts.

Tin Tetrachloride or *Stannic Chloride*, $SnCl_4$, was first mentioned by Libavius in 1605, who obtained it by distilling tin or its amalgam with excess of corrosive sublimate. It was termed by him *Spiritus argenti vivi sublimati*, but afterwards it received the name *Spiritus fumans Libavii*. For its preparation the process originally proposed by Libavius may be employed, or chlorine may be passed over tin foil, tin-plate scrap (p. 847), or fused tin placed in a retort. When the stream of chlorine is quick, and especially if the gas-delivery tube dips into the molten metal, an evolution of light and heat is observed. It may also be prepared by passing chloroform vapour over the heated dioxide.[3]

Tin tetrachloride is a colourless, thin, fuming liquid, which solidifies at $-33°$, has a specific gravity of 2·234 at 15°, and boils at 113·9°,[4] forming a colourless vapour having the normal specific gravity of 9·1997 (Dumas). At the boiling point it dissolves rhombic sulphur, yellow phosphorus, and iodine, and can be mixed in all proportions with bromine and carbon disulphide. When mixed with turpentine so much heat is evolved that the hydrocarbon takes fire. Its property of fuming in the air

[1] Marignac, *Ann. des Mines*, 1859, [5], **15**, 221.
[2] Emich, *Monatsh.*, 1904, **25**, 907.
[3] Renz, *Ber.*, 1906, **39**, 249.
[4] Thorpe, *Journ. Chem. Soc.*, 1880, **37**, 331.

depends on the fact that it absorbs atmospheric moisture. In 1770 Demachy observed that it solidified when brought into contact with one-third of its weight of water to form a crystalline mass termed *butter of tin.* Several distinct hydrates soluble in water may be produced, according to the quantity of water which is added. Thus the compound $SnCl_4,3H_2O$ is formed by exposing the anhydrous chloride to the action of moist air, or by the evaporation of its aqueous solution. This hydrate crystallises in monoclinic needles which melt at 80°, and on cooling again solidify to a crystalline mass. A second hydrate, having the composition $SnCl_4,5H_2O$, is obtained by the addition of a sufficient quantity of water to the anhydrous chloride, or by the gentle evaporation of the aqueous solution. It is deposited in opaque, acute, monoclinic prisms, which melt at a low temperature and again solidify to a crystalline mass. Lastly, large transparent, monoclinic crystals of the hydrate $SnCl_4,8H_2O$ are deposited in the cold from a dilute solution. On boiling a dilute aqueous solution of tin tetrachloride, stannic hydroxide is formed, and in very dilute solutions this precipitate forms spontaneously on standing.

Tin tetrachloride is employed by the dyer as a valuable mordant. Drebbel in Holland is said to have made the discovery that by help of this salt a permanent red dye can be obtained from cochineal. The dyers were formerly in the habit of preparing this mordant, known by the old names of tin-composition, physic, or dyer's spirits, by dissolving tin, together with sal-ammoniac or common salt, in nitric acid, or by dissolving tin in aqua regia, whence the solution was formerly termed nitro-muriate of tin. It is usual now for the dyers to employ the crystalline pentahydrate, $SnCl_4,5H_2O$, which is a commercial product known as *oxymuriate of tin.* It is also largely employed for weighting silk.

Anhydrous stannic chloride combines with ammonia to form a solid mass having the composition $SnCl_4(NH_3)_4$, which can be sublimed and is soluble in water without decomposition.[1] It can be obtained in crystals by evaporating the aqueous solution over sulphuric acid, but if it be allowed to stand for some days, or if the liquid be warmed, stannic hydroxide separates out in a gelatinous form. Tin tetrachloride combines also with many other chlorides to forms crystalline compounds,[2] such as

[1] Persoz, *Ann. Chim. Phys.*, 1830, **44**, 322.
[2] H. Rose, *Pogg. Ann.*, 1837, **42**, 517.

$SnCl_4,2SCl_4$. This is obtained by the action of chlorine on tin disulphide, and forms large, yellow crystals, which melt at a summer temperature, and decompose above 40°, with evolution of chlorine. If dry nitrous fumes are led into a solution of stannic chloride, the compound $SnCl_4,N_2O_3$ is deposited as a yellow, amorphous mass, and if this be sublimed or if the dry vapours from aqua regia be passed into the chloride, the compound $SnCl_4,2NOCl$ is produced, which crystallises in bright shining octahedra. If a solution of stannic chloride in chloroform be used, a white precipitate of $SnOCl_2,3SnCl_4,N_2O_5$ is obtained and this on heating yields a white sublimate of $SnCl_4,4NOCl$.[1] Stannic chloride also combines with phosphorus pentachloride to form the compound $SnCl_4,PCl_5$, which sublimes in glistening, colourless crystals, but when kept even in closed vessels falls to an amorphous powder. It has a peculiar, extremely pungent smell, and fumes strongly in the air. The compound $SnCl_4,POCl_3$ forms crystals which melt at 58°, and can be distilled at 180° without decomposition. This compound fumes strongly in the air, and is at once decomposed by contact with water.[2]

Like the fluoride, stannic chloride readily yields a series of double salts known as the *stannichlorides*, which present a similarity to the platinichlorides, but are less stable than the latter salts.[3] The free acid, H_2SnCl_6, is obtained in thin plates containing $6H_2O$ by saturating the pentahydrate, $SnCl_4,5H_2O$, with hydrochloric acid gas at 28° and cooling the resulting liquid to 0°.[4]

Ammonium Stannichloride, $(NH_4)_2SnCl_6$, separates as a crystalline powder when solutions of the two salts are mixed, and crystallises from dilute solution in small regular octahedra. It dissolves at the ordinary temperature in 3 parts of water. Its concentrated solution can be boiled without decomposition, but when diluted tin hydroxide separates out. It was formerly much used by the calico-printer under the name of *pink salt*, from its power of acting as a mordant for madder-red colours, but its use has been almost entirely superseded by the crystalline pentahydrated stannic chloride.

[1] Thomas, *Compt. rend.*, 1896, **122**, 32.

[2] Casselmann, *Annalen*, 1852, **83**, 257.

[3] von Biron, *J. Russ. Phys. Chem. Soc.*, 1904, **31**, 489; Bellucci and Parravano, *Atti R. Accad. Lincei*, 1904, [4], **13**, ii., 307; von Biron, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 963, 994, 1036.

[4] Engel, *Compt. rend.*, 1886, **103**, 213; Seubert, *Ber.*, 1887, **20**, 793.

Tin Tetrabromide or *Stannic Bromide*, $SnBr_4$.—Tin and bromine unite together with evolution of light and heat. The bromide is best prepared by adding bromine very slowly to strips of tin, the temperature being kept between 35° and 59°.[1] It is a white, crystalline mass, which fumes strongly on exposure to air and is easily soluble in water. It melts at 33° and boils at 201°. The specific gravity of the liquid is 3·349 at 35°, and its vapour density is 7·92.[2] It is easily soluble in cold water, forming a colourless liquid from which the hydroxide is deposited slowly on standing at the ordinary temperature and quickly on boiling. It yields crystalline *stannibromides* with the alkali bromides.

Tin Tetraiodide, SnI_4.—When tin and iodine are heated together, combination commences at 50°, and at a higher temperature heat and light are emitted. In order to prepare this compound, tin filings are first moistened with carbon disulphide, and then iodine is gradually added. It crystallises in red octahedra, melting at 146° and having a specific gravity of 4·696. Tin tetraiodide boils at 295°, but sublimes at as low a temperature as 180° in yellowish-red needles, very similar in form to those of ammonium chloride. It is soluble in carbon disulphide, absolute alcohol, ether, chloroform, and benzene, and is decomposed by water into hydriodic acid and stannic oxide.

If ammonia be led into a solution of tin tetraiodide in carbon disulphide, and at the same time the solvent be allowed to evaporate, a white substance, $SnI_4,8NH_3$, is formed. This same compound may also be formed by passing ammonia over the tetraiodide.[3]

Mixed Halogen Compounds of Tin.—Three stannic chlorobromides were thought by Besson to have been formed by the action of hydrogen bromide on stannic chloride, or of bromine on stannous chloride, whilst the action of iodine on stannous chloride was thought by Lenormand to yield the stannic chloroiodides, and on stannous bromide the stannic bromoiodides. These are fuming liquids or crystalline solids, and are decomposed by water with formation of stannic hydroxide. A list of these supposed compounds is given in the annexed table:

[1] Lorenz, *Zeit. anorg. Chem.*, 1895, **9**, 365.
[2] Carnelley and O'Shea, *Journ. Chem. Soc.*, 1878, **33**, 55.
[3] Ephraim and Schmidt, *Ber.*, 1909, **42**, 3856.

Formula.	Melting point.	Boiling point.	Specific gravity.
[1] $SnCl_3Br$	−31°	About 50° at 30 mm.	2·51 at 13°
[1] $SnCl_2Br_2$	−20°	About 65° at 30 mm.	2·82 at 13°
[1] $SnClBr_3$	1°	About 75° at 30 mm.	3·12 at 13°
[2] $SnCl_3I$	—	—	—
[2] $SnCl_2I_2$	—	About 191°	3·287 at 15°
[2] $SnClI_3$	—	—	—
[2] $SnBr_3I$	—	230—250°	—
[2] $SnBr_2I_2$	54°	225°	3·631 at 15°
[2] $SnBrI_3$	—	—	—

Auger,[3] however, has examined the freezing points of mixtures of $SnBr_4$ and SnI_4, and has found that they give a normal freezing point curve, with a eutectic at the composition $SnBr_{3\cdot2}I_{0\cdot8}$.

The supposed compound $SnBr_2I_2$, melting at 54°, is identical with an equimolecular mixture of $SnBr_4$ and SnI_4, and may be separated by a series of ten fractional crystallisations into fractions melting at 88° and 27°, of compositions $SnBr_{1\cdot2}I_{2\cdot8}$ and $SnBr_{2\cdot7}I_{1\cdot3}$ respectively.

It is quite possible that the same conditions obtain in the case of the other supposed mixed halogen compounds of tin.

Tin Disulphide or *Stannic Sulphide*, SnS_2.—This compound, crystallising in six-sided tablets or in gold-coloured, translucent scales having a specific gravity of 4·425, is used as a bronze powder for the purpose of bronzing articles of gypsum, wood, &c., and is known in commerce as mosaic gold. The discovery of this compound is usually ascribed to Kunkel. He does indeed speak of a sublimation of sulphide of tin and sal-ammoniac, but expresses himself so vaguely that it is impossible to recognise this compound from his description. It was well known in the eighteenth century under the names of *mosaic gold*, *aurum mosaicum*, or *musivum*. It was then prepared as it is at the present day by subliming a mixture of tin amalgam, sulphur, and ammonium chloride, and as it was supposed to contain mercury it was often employed as a mercurial medicine. Peter Woulfe in 1771 showed that it did not contain mercury, and described other methods for its production, according to which it is still prepared. Thus, for instance, it is obtained in the form of a fine pigment by heating 18 parts of tin

[1] Besson, *Compt. rend.*, 1897, **124**, 683.
[2] Lenormand, *J. Pharm.*, 1898, [6], **8**, 249 ; 1899, [6], **10**, 114.
[3] *Compt. rend.*, 1909, **149**, 860.

amalgam, containing 6 parts of mercury, with 6 parts of ammonium chloride and 7 parts of sulphur, when ammonium chloride, mercuric chloride, and stannous chloride sublime, and stannic sulphide remains behind in the form of golden-yellow scales. It is likewise prepared by heating tin monosulphide with 8 parts of mercuric chloride, or subliming tin filings with ammonium chloride and sulphur, and according to several other receipts given by Woulfe.[1] Pelletier believed mosaic gold to be a compound of sulphur with the highest oxidation product of tin, and Proust, who found that it could be obtained by heating stannous chloride or tin monoxide with sulphur, supposed it to be a compound of tin, sulphur, and a small quantity of oxygen. The exact composition was ascertained by J. Davy and Berzelius in the year 1812. The formation of mosaic gold from tin, sulphur, and ammonium chloride appears to take place according to the following equations (Gmelin):

(I.) $Sn+4NH_4Cl=(NH_4Cl)_2SnCl_2+H_2+2NH_3$
(II.) $2(NH_4Cl)_2SnCl_2+S_2=SnS_2+2NH_4Cl+(NH_4Cl)_2SnCl_4$.

When heated, a portion sublimes without decomposition, but the greater part is resolved into sulphur and monosulphide. It is not attacked by hydrochloric or nitric acid, but readily dissolves in aqua regia, as well as in caustic potash, when potassium stannate and potassium thiostannate are formed. If sulphuretted hydrogen be led into a solution of the tetrachloride a yellow precipitate is obtained. This consists of a mixture of tin disulphide and tin dioxide, and is readily soluble in the sulphides of the alkali metals, when the *thiostannates* are formed.

Thiostannic Acid.—When dilute hydrochloric acid is added to a solution of thiostannate, a yellow precipitate is obtained, which on drying forms an almost black powder possessing a brown streak and wax-like lustre, and having the composition H_2SnS_3. When heated in absence of air it yields the golden-yellow disulphide.[2]

Potassium Thiostannate, $K_2SnS_3,3H_2O$, is prepared by boiling a concentrated solution of potassium sulphide with the necessary quantities of sulphur and tin; it crystallises in colourless prisms. By a similar process the *sodium salt,* $Na_2SnS_3,2H_2O$, is obtained in yellow, vitreous, regular octahedra.[3] When sodium sulphide is fused with tin monosulphide and

[1] *Phil. Trans.*, 1771, **61**, 114. [2] Kühn, *Annalen*, 1852, **84**, 110.
[3] Ditte, *Compt. rend.*, 1882, **95**, 641.

sulphur, a black, crystalline mass is obtained, yielding a dark-coloured solution, which on concentration at a low temperature yields colourless crystals resembling gypsum, and having the formula $Na_4SnS_4,12H_2O$.

Ammonium thiostannate is formed by dissolving the sulphides in yellow ammonium sulphide, and may be precipitated by alcohol in unstable yellow tablets of the composition[1] $(NH_4)_2SnS_3,3H_2O$.

When mosaic gold is fused with iodine in absence of air, a crystalline mass of SnS_2I_4 is obtained, and this can be sublimed, or recrystallised from solution in carbon disulphide. It is decomposed by water into stannic oxide, sulphur, and hydriodic acid.

Stannic Oxysulphide, $Sn_2OS_3,11H_2O$.—This compound is obtained by allowing precipitated stannic sulphide to remain in contact with ammonia, filtering and acidifying the filtrate, or by digesting the sulphide with ammonium carbonate and acidifying the filtered solution. It is a white mass which is soluble in ammonia and gradually becomes yellow on keeping.[2]

Stannic Sulphate, $Sn(SO_4)_2$.—As already mentioned, tin dioxide dissolves in concentrated sulphuric acid, and from the solution two crystalline bodies may be obtained having the empirical formulæ $SnO_2,2H_2SO_4$ and SnO_2,H_2SO_4, which may be regarded as the normal sulphate, $Sn(SO_4)_2,2H_2O$, and the basic sulphate, $Sn(SO_4)_2,SnO_2,2H_2O$. Both of these are decomposed by water with separation of stannic oxide.

On mixing solutions of stannic acid in sulphuric acid, and calcium sulphate in sulphuric acid, and concentrating, regularly formed, colourless cubes are obtained of $Sn(SO_4)_2,CaSO_4,3H_2O$; similar salts are obtained with barium, strontium and lead sulphates.[3]

Stannic Nitrate, $Sn(NO_3)_4$, is obtained as a white powder by the action of 70 per cent. nitric acid on tin, but must be quickly removed, as it is rapidly converted into the hydrated dioxide. It is a white substance which is stable in presence of concentrated nitric acid at 90°, but is immediately decomposed at 100°.[4] It dissolves in water, but the solution is almost immediately decomposed with separation of hydrated stannic oxide.

[1] Stanek, *Zeit. anorg. Chem.*, 1898, **17**, 117.

[2] Schmidt, *Ber.*, 1894, **27**, 2739; see also *Chem. Centr.*, 1907, i., 397.

[3] Weinland and Kühl, *Ber.*, 1906, **39**, 2951; see also *Zeit. anorg. Chem.*, 1907, **54**, 259.

[4] Montemartini, *Gazz.*, 1892, **22**, 384.

Tin and Phosphorus.—When finely-divided tin is heated in the vapour of phosphorus, a silver-white, very brittle mass, having the composition SnP, is obtained. This has a specific gravity of 6·56, and dissolves readily in hydrochloric acid, but is not attacked by nitric acid. When phosphorus is thrown on to the surface of molten tin, combination also takes place. The compound containing the largest quantity of phosphorus which can thus be obtained has a silver-white colour, is not very brittle, and may be cut with a knife; it appears to possess the composition Sn_3P_2 (Pelletier).[1] If spongy tin, obtained by precipitating a tin salt with zinc, be brought into contact with such a quantity of phosphorus that one atom of the latter be present to nine atoms of the metal, a phosphide having the composition Sn_9P is obtained. The same compound is formed whenever any of the other phosphides containing more phosphorus is heated. This is a coarse, crystalline mass, which has the appearance of cast zinc. It melts at 370°, and is used for the preparation of phosphor-bronze.

Stannic Pyrophosphate is obtained by the action of phosphoric acid on stannic acid, and is insoluble in water and in nitric acid. This reaction is employed for the separation of phosphoric acid from other bodies. For this purpose a known quantity of tin foil is added to the nitric acid solution of the body under investigation, when the whole of the phosphoric acid remains behind with the metastannic acid.

Detection and Estimation of Tin.

400 When a small quantity of a tin compound is held in the reducing flame on charcoal, a malleable bead of metal is obtained, which easily dissolves in hot hydrochloric acid. This solution gives with a small quantity of mercuric chloride a white precipitate which becomes grey on boiling:

$$\text{(I.)}\ SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$$
$$\text{(II.)}\ SnCl_2 + Hg_2Cl_2 = SnCl_4 + 2Hg.$$

If one of the metallic globules be fused in a borax bead slightly tinted with cupric oxide and heated in the reducing flame, the bead will become of a red tint, due to the formation of cuprous oxide.

[1] See also Stead, *J. Soc. Chem. Ind.*, 1897, **16**, 200, 309; and Jolibois, *Compt. rend.*, 1909, **148**, 636.

Stannous salts yield a brown precipitate of stannous sulphide with sulphuretted hydrogen, which dissolves in ammonium sulphide containing polysulphides; the solution, on addition of an acid, deposits stannic sulphide. Ammonia and caustic alkalis give a white precipitate of stannous hydroxide, which is soluble in excess of the latter reagents. Stannous chloride gives a blue coloration with ammonium molybdate, and in this way 1 part of tin as stannous chloride may be detected in 1,500,000 parts of solution.[1]

Stannic salts yield a yellow precipitate of stannic sulphide with sulphuretted hydrogen, readily soluble in ammonium sulphide, and alkalis precipitate stannic hydroxide, which dissolves in an excess of the precipitant.

Zinc precipitates metallic tin from solutions of the tin salts in the form of glistening scales, or in a spongy or arborescent mass. The tin salts do not impart any colour to the non-luminous gas-flame, but the spark spectrum of the chloride exhibits two characteristic lines having wave-lengths of 4526 and 5631 (Lecoq de Boisbaudran). These same lines are seen together with others in the spark spectrum of the metal, the most brilliant of the tin lines being as follows (Thalén): 6452, 5798, 5631, 5588, 5563, 4526.

In the processes of qualitative analysis tin is obtained together with those metals which are precipitated by sulphuretted hydrogen in an acid solution. To separate tin from these the well-washed precipitate is treated with yellow ammonium sulphide, filtered, and the filtrate acidified with cold dilute hydrochloric acid. The precipitate may contain, beside stannic sulphide, the sulphides of arsenic and antimony. After it has been well washed with water, it is digested with solid ammonium carbonate to dissolve the sulphide of arsenic. The residue is then dissolved in concentrated boiling hydrochloric acid, the solution boiled with metallic copper, and the liquid tested for stannous chloride with mercuric chloride (see also under antimony).

Tin may be estimated as the oxide. If the metal or one of its alloys be under examination, it is oxidised with pure, tolerably strong nitric acid, and the well-washed residue ignited. From solution it is precipitated with ammonia as the hydroxide, but if it be present in the form of stannous salt it must be first oxidised with chlorine or hydrochloric acid and

[1] Longstaff, *Chem. News*, 1899, **80**, 282; Rogers, *J. Amer. Chem. Soc.*, 1900, **22**, 220.

potassium chlorate. The precipitate obtained by ammonia is then dissolved in the smallest quantity of hydrochloric acid and heated with a concentrated solution of sodium sulphate, when the hydroxide is again precipitated, and this is not gelatinous, and may therefore be easily washed (Löwenthal). When tin sulphide is obtained in the separation of tin from the other metals, it can be gradually converted into stannic oxide by gentle roasting and subsequent ignition.

Tin is frequently estimated by volumetric methods, the processes depending on the oxidation of stannous chloride to stannic chloride by means of standard solutions of ferric chloride or iodine.

The electrolytic method has been employed for estimating tin as the metal, the process being carried out in the presence of ammonium oxalate or some other organic salt.[1] It may be deposited also from solutions in ammonium sulphide.

Atomic Weight of Tin.—The early determinations of the atomic weight of tin were made by oxidising the metal to the dioxide, but the numbers obtained varied considerably. Thus Berzelius[2] found the number 117·65, and Mulder and Vlaanderen[3] 116·3, whilst a later determination by the last named gave the higher value 118·16. Dumas[4] by the same method obtained the number 118·06. The most reliable determination is, however, that of Bongartz and Classen,[5] who employed four different methods, namely, the oxidation of pure tin with nitric acid, and the electrolysis of potassium stannichloride, ammonium stannichloride, and stannic bromide. The average of the most trustworthy experiments gave the number 119·0, which is now (1913) adopted.

LEAD.

Pb (Plumbum) = 207·10.

401 The first mention of lead occurs in the well-known passage in the Book of Job, Chap. XIX, and it is mentioned also in the Book of Numbers, Chap. XXXI, as a portion of the spoil taken from the Midianites. It is found under the name of óphéret,

[1] Engels, *Ber.*, 1895, **28**, 3182; Hollard, *Compt. rend.*, 1897, **124**, 1451; Fischer, *Ber*, 1903, **36**, 2348; &c.

[2] *Pogg. Ann.*, 1826, **8**, 177.

[3] *J. pr. Chem.*, 1849, **49**, 35.

[4] *Ann. Chem. Pharm.*, 1860, **113**, 26.

[5] *Ber.*, 1888, **21**, 2900.

derived from the word áphár, signifying to have a grey appearance. In the oldest Greek translations of the Old Testament the word μόλιβος occurs, and this as well as the word μόλυβδος undoubtedly refers to lead. It appears that no exact distinction was drawn between the metals lead and tin during the time of the Israelites, but we find that Pliny points out a distinction between these two metals, inasmuch as he gives the name of *plumbum nigrum* to lead, whilst tin is designated as *plumbum candidum* (p. 842). Lead was known to the ancient Egyptians, as lead plates have been found in the Temple of Rameses III.

It has already been stated that the seven metals known to the ancients were supposed to be in some way connected with the seven heavenly bodies which were then known to belong to our solar system. Dull, heavy lead was apportioned to Saturn, and this metal is designated in the writings of the alchemists by the sign ♄.

Lead is seldom found in the free state in nature. Native lead does, however, occur in small quantities in certain lead ores, and in volcanic tufa. The oxides of lead are found in the form of rare minerals, the yellow oxide, PbO, and the red oxide or red lead, Pb_3O_4. The commonest ore of lead is galena or lead sulphide, PbS; this is very widely distributed, generally occurring together with quartz, calc-spar, fluor-spar, and heavy-spar, in the older as well as in the more recent strata, and in almost every part of the world. Thus in Cornwall it occurs in veins in the coarse argillaceous schist, provincially termed killas; in Derbyshire, Cumberland, Northumberland, and Yorkshire, it is found in mountain limestone; in Cardiganshire and Montgomeryshire it occurs in the Lower Silurian; and the chief deposits in the United States likewise occur in this same formation. Again, at Sala in Sweden, it is found in granular limestone, and in Freiberg in a schistose gneiss, older than the carboniferous system. Sulphide of lead also occurs in combination with the sulphides of antimony and copper in the minerals zinckenite, $PbSb_2S_4$, and bournonite, $CuPbSbS_3$. In addition to these ores, lead carbonate occurs as the mineral cerussite, $PbCO_3$, found in some localities, as in the neighbourhood of Aix-la-Chapelle and of Santander in Spain, in sufficient quantity to be worked. It is also found in the lead mines of Cornwall and Devonshire, in Yorkshire, at Leadhills in Scotland, and at Seven Churches in County Wicklow. Other naturally occurring compounds of lead are the basic chloride,

occurring as the minerals matlockite, Pb_2Cl_2O, and mendipite, $Pb_3Cl_2O_2$, and the sulphate of lead or anglesite, $PbSO_4$, found associated with galena and carbonate of lead at Leadhills and in other localities. Again, we have a basic sulphate called lanarkite, $PbO,PbSO_4$; leadhillite, $PbSO_4,3PbCO_3$; phosgenite, $PbCl_2,PbCO_3$; stolzite or lead tungstate, $PbWO_4$; wulfenite or lead molybdate, $PbMoO_4$; crocoisite or lead chromate, $PbCrO_4$; pyromorphite or lead phosphato-chloride, $3Pb_3P_2O_8,PbCl_2$; mimetesite or lead chloro-arsenate, $3Pb_3As_2O_8,PbCl_2$; as well as compounds of lead with the rarer elements, such as selenium, tellurium, selenic acid, vanadic acid, &c.

By far the greater quantity of the total lead brought into the markets of the world is derived from galena.

402 *Smelting of Lead.*—Lead is an easily reducible metal requiring but simple processes for its production, and it was produced in England during the Roman occupation in a variety of localities. Numerous pigs of Roman lead have been found bearing Latin inscriptions. Whether lead was reduced in England before this period appears doubtful; the remains of rude furnaces in which lead ore was smelted in early times are, however, found in Derbyshire and elsewhere, and are termed *boles* by the inhabitants. In these furnaces the heat was not urged by an artificial blast of air, but piles of stone were built on the western brow of some eminence so as to employ the natural currents of air on mountainous places. A mixture of ore and charcoal was introduced into the interior of these furnaces, the lead being run out at the bottom after the operation.

The form of furnace next employed was the *ore-hearth*, a small, rectangular blast-furnace blown by bellows worked by means of a water wheel.[1] This furnace is still in use in certain localities.

About the middle of the eighteenth century lead smelting in reverberatory furnaces appears to have been introduced into England from Flintshire, where it was in use in the year 1698.

Three distinct processes are employed for lead smelting. The first of these, known as the *air reduction process* (Percy), is employed when the ore consists mainly of galena, and is free from silica and the sulphides of other metals. The second, or

[1] See H. L. Pattinson, "Description of Lead-Smelting in the North of England." *Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-on-Tyne*, vol. 2, part i.; also J. J. Brown, jun., "Lead Smelting in the Ore-Hearth," *Trans. Am. Inst. Min. Eng.*, 1911, **42**, 402.

carbon reduction process, is employed for less pure ores and consists in the roasting of the ore and the subsequent reduction of the lead oxide by carbonaceous matter. The third process is known as the *precipitation process*, the reduction of the lead being effected by metallic iron; this is chiefly practised in France, Germany, Spain, and North America, where the ore contains other metals, such as copper, antimony, and arsenic. It is however, to be remembered that two or even three of the above processes are often worked in the same furnace with the same charge of ore.

In the *air reduction process* the galena is roasted in a reverberatory furnace until a portion of the sulphide is converted into oxide and sulphate; the temperature is then raised, when metallic lead is formed together with sulphur dioxide. The following reactions are usually given as representing the interaction of the unaltered lead sulphide with the oxide and sulphate:

$$2PbO + PbS = 3Pb + SO_2.$$
$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

In presence of an excess of sulphur dioxide, however, lead is partially reconverted into sulphide and sulphate:[1]

$$2Pb + 2SO_2 = PbS + PbSO_4.$$

The reverberatory furnaces used for the English process of lead smelting are of two kinds, the Flintshire furnace and the flowing furnace. The difference between these is that in the first the slag is raked out in pasty lumps, whereas in the flowing furnace the slag is tapped out in the molten state and termed run-slag. The reaction which takes place during reduction is identical in both cases.

Fig. 182 shows the construction of the Flintshire furnace. The usual charge of ore is 20 cwt. This is introduced by means of a hopper (T) in the arch of the furnace. The hearth of the furnace (B) is hollowed out as shown in the figure to permit the lead to flow through a tapping hole into an iron pot placed in front of the furnace. The charge is evenly spread over the surface and gently heated, the ore being well rabbled at intervals, and the temperature carefully regulated by opening or closing the various doors, so as to maintain the mass as hot as is possible without causing it to clot together; a por-

[1] Jenkins and Smith, *Proc. Chem. Soc.*, 1897, **13**, 104; Schenck and Rassbach, *Ber.*, 1907, **40**, 2185, 2947.

tion of the sulphide is oxidised to oxide and sulphate, and the mass thus prepared for the following stage of the operation. During this part of the process the skimmings from the lead run off from the previous operation, which consist chiefly of lead containing a little sulphide, are added, and are quickly acted on by the lead oxide and sulphate with formation of metallic lead, which is run off from the tap-hole and contains more silver than the subsequent portions of the metal. After about two hours the temperature is raised to a bright red heat, the metal being formed in quantity, whilst from time to time, in addition to stirring the mass, a small quantity of lime is added to stiffen the unreduced portion. This part of the process extends over an hour, and then for three-quarters of an hour the temperature is further raised and an additional

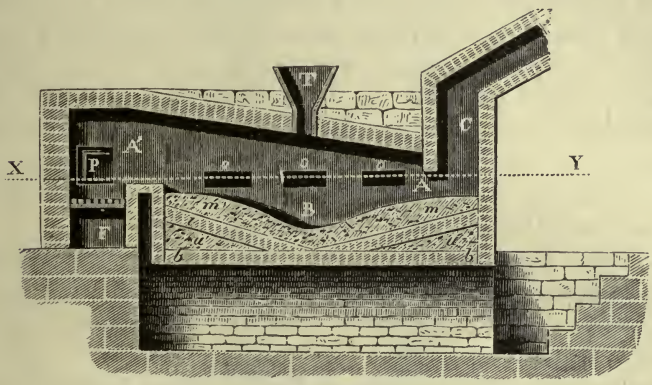


Fig. 182.

small quantity of lime added, which besides lessening the fusibility of the mass also liberates any lead oxide, which may have combined with the silica, and allows it to be reduced by the lead sulphide. Finally, the furnace is raised for three-quarters of an hour to the highest attainable temperature and a sufficient quantity of lime added partially to solidify the slag, which is raked out, and the lead run off from the tap-hole in the usual manner.

The *grey slag* obtained may contain as much as 40 per cent. of lead, and is further worked up in the slag-hearth, which is a small shaft furnace, or may be mixed in with the charge for the larger blast furnaces.

Reduction of Lead in Blast Furnaces.—This is the method now most generally adopted, as it is suitable for any class of ore and

the percentage of lead may be much lower than that necessary for the other methods, whilst the presence of silica to a certain extent is not disadvantageous. For ores such as those which occur in the Harz, where the galena is mixed with iron and copper pyrites, zinc blende, fahl-ore, bournonite, and zinckenite, the blast furnace method gives the best results, and this is suitable also for the reduction of the oxides or carbonates of lead. The process for sulphide ores consists first in roasting to get rid of sulphur and then smelting the roasted ore with fluxes and reducing agents in the blast furnace. The roasting is effected in heaps, shaft furnaces or reverberatory furnaces, and the latter may be worked by hand or mechanically.

Several new methods of roasting galena have been introduced, in which the ore is mixed with lime, gypsum, oxide of iron or other material, damped and fed on to a small fire in a converter-shaped vessel, through which air is blown,[1] or fed on to some type of sintering machine such as is used in the various Dwight-Lloyd[2] processes for down-draft roasting. The chief advantage of these processes lies in the fact that the product obtained is very suitable for blast-furnace treatment, but besides this the cost is less, the losses of metal are less, and the production of fine material is greatly reduced.

The blast furnace mostly used for lead and silver-lead smelting is rectangular in plan, about 44 inches wide and 144 inches long inside at the tuyere level. Fig. 183 is a section of such a furnace which comprises a crucible portion A, a shaft B, extending from the crucible to the feed-floor C, and a stack from the feed-floor upwards. The furnaces are water-jacketed about the lower portion or bosh of the shaft, these jackets being made of cast iron or of steel, and through them water circulates continually. These jackets are shown at D, and through the side jackets the tuyeres E pass into the furnace. The shaft above these jackets is lined with fire-brick.

An Arents syphon tap is often fitted to the crucible portion of these furnaces for continuously drawing off the lead. When the ores contain copper the roasting is not carried so far, a certain amount of sulphur being left in the ore to combine with the copper for the formation of a cupriferous matte, and in this

[1] *Mineral Industry*, 1905, **14**, 402; see also "Lead-Smelting and Refining," by W. R. Ingalls, published by the *Engineering and Mining Journal*, 1906; for "The Theory of Blast Roasting of Galena," see Bannister, *Trans. Inst. Min. and Met.*, 1912, **21**, 346.

[2] *Report of Seventh Internat. Cong. App. Chem.*, 1909, III, *A*, 20.

case a certain amount of unaltered lead sulphide will always be present in the matte. The furnace charge consists of a mixture of roasted ore, carbonaceous fuel, generally coke or a mixture

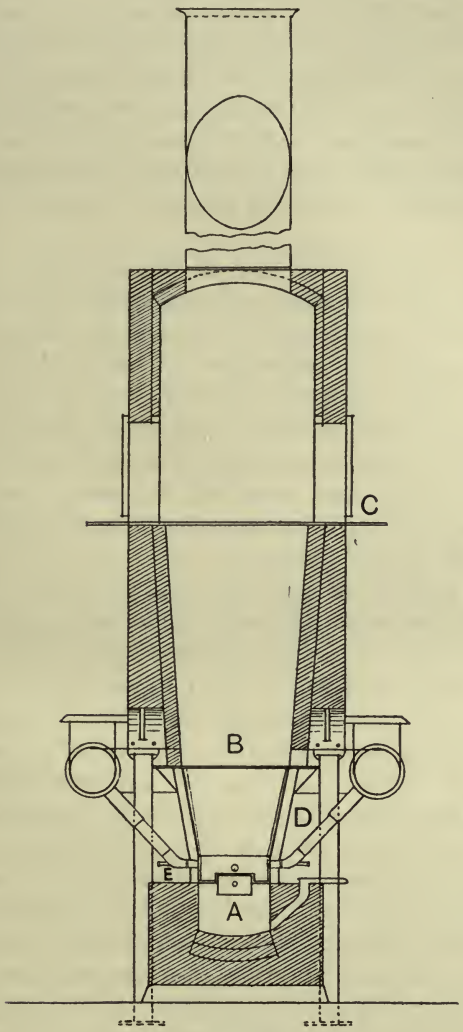


Fig. 183.

of coke and charcoal, old slags and fluxes. The fluxes most used are ferruginous ores, often carrying silver or gold, which is collected partly in the lead and partly in the matte if this be also formed, ferruginous slags containing an excess of ferrous

oxide, and sometimes lime or limestone. The slag should contain between 30 and 35 per cent. of ferrous oxide, between 10 and 30 per cent. of lime, and between 30 and 50 per cent. of silica. The lead present in the form of oxide is reduced partly by the carbon monoxide in the gases and partly by solid carbon; that present as sulphide, by iron, generally formed by reduction of the oxide of iron present in the charge. Any silicate present is reduced by the action of carbon in the presence of ferrous oxide or lime, and any lead sulphate present is reduced by reaction with sulphide, or is converted into sulphide by the action of carbon and this sulphide reduced by metallic iron.

Softening of Lead.—The lead produced in these processes is hard, owing to the presence of small quantities of antimony, arsenic, copper, zinc, iron, tin, bismuth, and sulphur, and it is necessary to remove these in order to render the lead marketable. Silver is also generally present and is removed by special processes, which are described later, and which enable the silver to be recovered. It is also necessary to remove impurities before desilverisation, as copper, antimony and arsenic interfere with the Pattinson process, and these, together with nickel and cobalt, interfere with Parkes' process.

For the purpose of removing the impurities, the lead is melted in a reverberatory furnace at a low temperature. Copper forms an alloy with some of the lead which is less fusible than lead itself and this separates out as a scum on the molten lead and may be removed; all the other commonly occurring impurities except bismuth are more readily oxidised than lead and are oxidised in the furnace together with a portion of the lead, the mixed oxides forming a dross on the surface which is removed from time to time. Bismuth cannot be got rid of in this manner, but it is concentrated with the silver in the Pattinson process for desilverisation. The hearths of modern reverberatory furnaces for the softening of hard lead consist of wrought iron pans lined with two thicknesses of firebrick and are often water-jacketed at the sides to diminish the corrosive action of the oxides formed on the material composing the hearth.

Condensation of Lead Fume.—During the smelting processes a large amount of lead fume is carried away in suspension in the waste gases from the furnaces, and many devices have been introduced for condensing and collecting these fumes, for subsequent treatment. In many works the arrangement con-

sists merely in having very long flues between the furnaces and the chimney, the amount of condensation depending on the length of the flue. In other works more complete condensation is effected by arrangements for lowering the velocity of the gases, by first passing the exit gases through large chambers containing baffle plates, and then through iron flues cooled by the air. Other methods for condensing the fume consist of using a water spray or causing the gases to pass through layers of water on their way to the chimney. "Bag houses" are largely used for the condensation of lead fume; in the use of these, the cooled gases are forced through canvas or twill bags on their way to the chimney.

403 *Desilverisation.*—Ordinary lead obtained by any of the above-mentioned processes always contains silver, and a very considerable proportion of the silver which now comes into the market is obtained from argentiferous galena. In former times the only process by which this silver could be extracted was cupellation, by which the whole of the lead is oxidised, whilst metallic silver remains behind. The oxide has then to be again reduced to metallic lead. It is, however, generally admitted that the process of cupellation cannot be economically carried on in the case of lead which contains less than 150 oz. of silver to the ton, and consequently, as very large quantities of lead are brought into the market containing smaller quantities than this, a large portion of this silver was lost until Hugh Lee Pattinson in the year 1833 obtained a patent for an improved method of separating silver from lead, which soon came into general use and by which large quantities of silver are now extracted from lead.

This method depends upon the fact that if lead containing a small quantity of silver be melted, and the melted mass allowed to cool, a point is reached at which pure lead begins to crystallise out. If the crystals of lead which are thus formed be then withdrawn from the remainder of the metal, and this process continued until the greater part of the lead has been separated, it is found that the liquid which remains contains most of the silver. In order to render this process economical the lead requires to be repeatedly crystallised in a series of iron pots, the lead rich in silver gradually accumulating towards one end of the series, whilst the desilverised or market lead is obtained at the other end.

The melted lead is first thoroughly skimmed, then the fire is

withdrawn and the lead allowed to cool, care being taken to break off and mix with the liquid mass any portion that may solidify on the sides of the pot. When the temperature reaches a certain point small crystals of lead begin to form, and at this point the whole mass of metal is continually stirred with an iron rod, whereby the crystals sink to the bottom of the pot and accumulate in considerable quantity. A perforated ladle is now introduced by means of which the crystals are removed. The operation is thus carried on in successive stages until two-thirds or even seven-eighths of the original lead is removed from the pot. By this means in an actual working 846 cwt. of original lead was separated into 36 cwt. of rich lead containing 160 to 170 oz. of silver per ton, and 810 cwt. of poor lead containing 7 to 10 dwt. of silver per ton. The silver is then extracted from the rich lead by the process of cupellation (p. 446).

A modification of the Pattinson process, known as the Luce-Rozan process, is now frequently adopted in place of the original method. For this only two pots are necessary, viz., an upper or melting pot, and a lower or crystallising pot. The former holds about 7, and the latter about 21 tons.

The mode of working the plant is as follows[1]: The crystallising pot may be supposed to contain 14 tons of lead crystals from a previous operation, and the melting pot 7 tons of lead of similar silver content, already melted; a moderate fire is set away in the fire-grate of the crystallising pot, and the contents of the melting pot skimmed of their dross; the hot lead from the latter is then run on the warm crystals in the crystallising pot, and with the aid of the moderate fire already referred to, the whole contents of this pot (now 21 tons) are rapidly melted and brought into a working condition, when the charge is carefully skimmed; the melting pot is at the same time charged with 7 tons of lead from a previous operation containing one half the amount of silver in the lead then being worked up, as this will be the assay of the crystals resulting from the operation about to be performed in the crystallising pot. The fire under the latter is then drawn, and steam at fifty to fifty-five pounds pressure per square inch admitted and distributed evenly by means of a baffle plate. To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of the lead, the crystallisation being more perfect than in the old

[1] Cookson, *Trans. Newcastle Chem. Soc.*, 1878.

Pattinson process. As soon as two-thirds of the lead has crystallised out, the rich liquid lead is tapped off, the crystals being retained in the pot by means of perforated plates. The liquid lead is run into moulds and awaits its turn for further treatment. The proportion of silver in the crystals is thus reduced to one half, whilst that in the liquid run off is doubled, and this process of recrystallising is repeated as in Pattinson's process, until the crystals are sufficiently poor in silver not to require further treatment, and the rich lead is worked up until its silver content is of the standard fit for cupellation.

This process has the advantage over that of Pattinson that a great saving is effected in fuel and the cost of labour, and also that, except in the case of very hard lead, no further softening process is necessary. The original outlay and expenses for repairs are, however, considerably greater.

Another process for desilverising lead is known as Parkes' or Karsten's zinc process. Molten lead and zinc do not mix in all proportions, lead being capable of taking only 1·6 per cent. of zinc, whilst zinc takes only 1·2 per cent. of lead, and Karsten, in 1842, concluded from experiments which he made on the subject that lead gives up all the silver which it contains if melted with zinc, but he did not apply this conclusion to practical metallurgy. In the year 1850 Alexander Parkes, of Birmingham, patented a process for extracting silver from lead by the above-mentioned reaction. For a ton of lead containing 14 oz of silver, 22·4 lbs. of zinc are needed and a proportionate amount if more silver be present. The alloy of zinc and silver rises to the surface during cooling, and when it solidifies it is withdrawn by means of a perforated ladle. In order to remove the small quantity of zinc which is dissolved in the lead, the mixture is heated to dull redness and steam blown through, the zinc being thereby oxidised, whilst the main portion of the lead remains behind in the marketable state. The zinc-silver alloy is first heated to a temperature slightly above the melting point of lead to liquate as much of the latter as possible, and the residue is heated with carbon in a crucible retort, whereby the zinc is distilled off and collected, the residual rich silver-lead alloy being cupelled in the usual manner.

Gold and copper, which sometimes occur in market lead, can be separated from it in the same way, inasmuch as these metals alloy with zinc even more readily than does silver, and this process has been satisfactorily carried out in England by Baker

A similar method is employed in the Harz; the lead is there melted with 0·16 per cent. of zinc, and the alloy is obtained as a scum on the surface, having the composition:

Pb	Zn	Cu	Ag
89·46	5·78	4·52	0·243

On a second addition an alloy having the following composition is obtained:[1]

Pb	Zn	Cu	Ag
91·05	5·21	3·50	0·238

Market lead almost always contains traces of antimony, copper and iron, and occasionally of zinc, nickel and bismuth, whilst the silver which it contains varies from one part in 40,000 to one part in 200,000, but since the introduction of the method of desilverising by zinc and purification by steam the purity of the commercial lead has very much increased.

An analysis of desilverised and refined lead of the Pennsylvania Lead Co.[2] gave the following results:

Antimony	0·00051 per cent.
Copper	0·00007 „
Iron	Traces
Zinc	0·00038 „
Silver	0·00042 „
Sulphur	0·00018 „

showing a total impurity of only 0·00156 per cent.

Electro-refining of Lead.[3]—Various attempts have been made from time to time to refine lead by an electrolytic process, but until Betts invented his process in 1901, no great success was attained. In this process, the electrolyte consists of lead fluosilicate solution; the anodes are cast of the crude lead and the cathodes of pure lead. In order to obtain solid deposits of lead, the use of addition agents to the electrolyte is necessary; and in this process gelatine is mostly used, in the proportion of 1 part of gelatine to 5,000 parts of solution. The impurities remain in the anode slime, and pure lead is deposited at the cathode, as shown by the following table:

[1] Rammelsberg, *Ber. Entw. Chem. Ind.*, 935.

[2] *Trans. Amer. Inst. of Mining Engineers*, 1874, **3**, 322.

[3] See *Lead Refining by Electrolysis*, by A. G. Betts (John Wiley & Sons, 1908).

	Cu	Bi	As	Sb	Ag	Pb
Crude lead	1·40	0·14	7·4	4·0	0·64	87·14
Pure lead	0·001	0·0022	0·0025	0·0017		
Anode slime	9·3	0·52	44·58	25·32	4·7	10·3

The following table shows the production of lead in 1911, by the chief lead-producing countries in metric tons:[1]

Australasia	19,352 tons
Belgium	30,800 „
France	23,000 „
Germany	161,287 „
Italy	16,700 „
Mexico	124,605 „
Spain	171,000 „
United Kingdom . . .	18,100 „
United States	363,829 „

404 *Chemically pure lead* is prepared according to Stas[2] as follows:—A solution of acetate of lead is heated in a leaden vessel in contact with thin sheet lead to a temperature of from 40° to 50° in order to precipitate silver and copper. The filtrate is then poured into pure, very dilute sulphuric acid, and the lead sulphate formed carefully washed with a solution of ammonium carbonate and ammonia, and thus converted into lead carbonate. A portion of this is then converted into lead oxide by carefully heating in an platinum basin, whilst to the remaining portion pure dilute nitric acid is added in such quantity that a portion of the carbonate remains undissolved. The oxide of lead is then added to the boiling solution of the nitrate in order to precipitate traces of iron, and the filtered solution poured into one of pure ammonium carbonate. The precipitated lead carbonate is then reduced by means of potassium cyanide, and the metal thus formed fused a second time with the cyanide, when it assumes in the molten state a convex surface like mercury.

Lead can easily be crystallised in the form of regular octahedra by melting, allowing the molten metal partially to solidify, and pouring off the portion which is still liquid. Similar crystals are obtained by the electrolytic decomposition of solutions of lead salts using a strong current, but with weak currents plates belonging probably to the monoclinic system are formed. It

[1] *Mineral Industry*, 1911, **20**, 451. [2] *Bull. Acad. roy. Bely.*, 1860, **10**, 295.

is also deposited at the cathode by the electrolysis of dilute sulphuric acid with lead electrodes, sometimes in the spongy form consisting of microscopic needles, and sometimes in plates.[1] Similar crystals to these separate out in bright shining arborescent forms, known as the lead tree, if a piece of zinc be hung up in a solution of lead acetate. Lead has a specific gravity of 11·254, or, after it has been poured into water, of 11·363. On hammering it cracks and becomes lighter, but if it be pressed it attains a specific gravity of 11·388. Lead that has been distilled in vacuo has the specific gravity 11·3415, and this after compression becomes 11·3470.[2] It is soft and tough, may be cut with a knife, and leaves a streak upon paper. It can easily be rolled out to thin foil, but it cannot be drawn out into fine wire. When melted repeatedly it becomes hard and brittle, which is probably due to the formation of a small quantity of oxide. On the large scale this oxide may be removed by poling or stirring up the molten mass with a pole of green wood. The presence of antimony, zinc, bismuth, arsenic, and silver increases the brittleness of lead. Lead belongs to the class of white metals, though it has a decidedly bluish-grey tint indicated by the expression lead-grey. A freshly cut surface possesses a bright lustre, which, however, soon becomes dull from superficial oxidation. By the electrolysis of lead nitrate Wöhler obtained a deposit on the negative pole of crystallised leaflets of lead possessing a red colour like that of copper. These did not dissolve in dilute acids, whilst they were soluble in hot nitric acid, and, on dissolving, the colour resembled that of copper to the last moment.[3] Lead melts at 327°, and begins to volatilise at a bright red heat, boiling rapidly before the oxy-hydrogen blowpipe. It cannot, however, be distilled in closed vessels like zinc, although when zinc is extracted from ores containing lead, the vapour of zinc is mixed with vapour of lead, and a considerable portion of the loss experienced in the ordinary processes of lead smelting is due to this cause.

Lead has been obtained in the colloidal form by reducing a solution of the dichloride with hydrazine hydrate in the cold.[4]

[1] Elbs and Rixon, *Zeit. Elektrochem.*, 1903, **9**, 265; Haber, *Zeit. anorg. Chem.*, 1898, **16**, 438.

[2] Kahlbaum, Roth, and Siedler, *Zeit. anorg. Chem.*, 1902, **29**, 177.

[3] *Ann. Chem. Pharm. Suppl.*, 1863, **2**, 135.

[4] Gutbier, *Zeit. anorg. Chem.*, 1902, **31**, 448.

Metallic lead is largely employed in the arts for a great variety of purposes on account of its softness and pliability, its low melting point, the difficulty with which it undergoes oxidation at ordinary temperatures, and the fact that it withstands the action of water and of many acids better than most of the common metals.

The most important alloys of lead are those which it forms with tin, which have been described under that metal (p. 850).

COMPOUNDS OF LEAD.

Lead and Oxygen.

405 Lead forms five compounds with oxygen:

Lead suboxide, Pb_2O,
Lead monoxide, PbO,
Lead sesquioxide, Pb_2O_3,
Red lead, Pb_3O_4,
Lead dioxide, PbO_2.

The most important of these is the strongly basic monoxide, which corresponds to the chief series of salts, in which lead is divalent. The dioxide acts as a weak basic oxide towards strong acids, as an acidic oxide to strong bases, and also behaves in many respects as a peroxide. The sesquioxide and red lead are probably salts formed by the combination of the basic monoxide and the acidic dioxide (p. 889).

Lead Monoxide, PbO.—This compound was known to the ancients, as it is formed when lead is heated in contact with the air, and is, therefore, produced in various metallurgical processes. The different forms of this compound were, however, regarded as different substances, giving rise to the names *plumbum ustum*, *scoria plumbi*, *scoria argenti*, *galena*, *μολύβδαινα*, *λιθάργυρος*, &c. When lead is heated to its point of volatilisation in the air, it takes fire and burns with a white light, yielding this oxide, which formerly received the name of flowers of lead or *flores plumbi*. Lead, when heated in the air, becomes covered with a grey film, and if the surface be continually renewed, becomes wholly converted into lead-ash, a yellowish-grey, pulverulent mixture of metallic lead and yellow monoxide, which, if heated in the air for a longer time, is wholly converted into the

latter. This yellow oxide is termed *massicot*, whilst the other form of lead monoxide, termed *litharge*, is obtained at a temperature at which the oxide fuses, solidifying to a scaly shining mass sometimes of a yellow tint, sometimes rather inclined to red.

Crystallised oxide of lead also occurs in nature as a mineral found near Vera Cruz (Nöggerath). The crystals may be artificially obtained by allowing litharge to cool slowly; it forms rhombic octahedra, which are sometimes also found as a deposit in the lead furnaces (Mitscherlich), and red tetragonal crystals may also be obtained (Geuther). Lead oxide possesses a colour varying from lemon-yellow to reddish-yellow, and on heating assumes a brownish-red tint. Its specific gravity at 4° is 9·36 (Joule and Playfair). It is reduced to the metallic state by carbonic oxide at 100°, by hydrogen at 310°, and by carbon [1] in an atmosphere of nitrogen at 550°. Litharge is largely used in the arts, especially for the manufacture of flint glass, and as a glaze for earthenware; it is used also for the preparation of red lead, lead acetate, lead nitrate, white lead, lead plaster, and drying oils. Commercial litharge contains carbon dioxide and water absorbed from the air, but they may be removed by ignition. Not infrequently it contains small quantities of iron oxide and copper oxide, the latter easily removable by ammonia.

Basic Lead Hydroxide, $Pb_2O(OH)_2$.—This substance is obtained as a white precipitate by the action of air and water free from carbonic acid upon the metal, or is thrown down as a white precipitate on the addition of ammonia or a fixed alkali to a lead salt; this, however, dissolves in a large excess of the reagent and the solution contains a *plumbite*, H·PbO·OR, in which the normal hydroxide acts as a weak monobasic acid.[2] The basic hydroxide is obtained in colourless, tetragonal crystals by exposing a cold solution of lead monoxide in caustic potash to the air, the carbon dioxide in the latter converting the caustic potash into potassium carbonate.

The compound $Pb_3O_2(OH)_2$ is formed according to Payen as follows:—100 parts of a solution of basic acetate of lead, $Pb_3O_2(C_2H_3O_2)_2$, saturated at 16°, are added to 50 volumes of cold water which has previously been well boiled: a mixture of 20 parts of ammonia and 30 parts of boiled water is then added, and the solution allowed to stand at a temperature of

[1] Doeltz and Graumann, *Metallurgie*, 1907, **4**, 420.
[2] Hantzsch, *Zeit. anorg. Chem.*, 1902, **30**, 289.

25—30°, when the above hydroxide separates out in glittering octahedra.

At 130° lead hydroxide loses a portion, and at 145° the whole, of its water, being then converted into lead oxide. The hydroxides of lead as well as the oxide turn moistened red litmus paper blue, as they are somewhat soluble in water. They act as strong bases but also combine with certain basic oxides. Thus when lead oxide is fused with the alkalis, alkaline earths, and other metallic oxides, a glass is formed, and, in consequence of this, lead oxide attacks clay crucibles. It dissolves also in caustic potash and soda as well as in lime and baryta water, yielding yellow liquids. The calcium compound is slightly soluble in water, and crystallises in white needles on cooling (Berthollet, Karsten).

Lead Suboxide, Pb_2O, is formed when lead oxalate is heated in an atmosphere free from oxygen to a temperature below 300° (Dulong):

$$2PbC_2O_4 = Pb_2O + CO + 3CO_2,$$

or when lead oxide is reduced by CO at 300°.[1] It is a black, velvety powder of specific gravity 8·342 at 18° (Tammann),[2] which, when heated in absence of air, or treated with caustic soda or acids, is decomposed into the metal and the monoxide. When lead is melted in the air the surface becomes covered first with a grey film, which, according to Berzelius, consists of the suboxide. The suboxide has by some been considered to be an intimate mixture of finely-divided lead and the monoxide. Against this view, however, is to be placed the fact that mercury does not dissolve metallic lead from this grey powder, whilst a solution of sugar, which readily dissolves lead monoxide, does not take up any from this substance. After heating, dilute acetic acid or a solution of sugar does dissolve out lead oxide, whilst metallic lead remains behind in the coherent state. Cold 10 per cent. sodium hydroxide decomposes it, forming sodium plumbite and metallic lead.

Lead Sesquioxide, Pb_2O_3, is formed when a solution of sodium hypochlorite is carefully added to a cold caustic potash solution of lead oxide (Winkelblech), or when a solution of red lead in acetic acid is precipitated by very dilute ammonia. It is a reddish-yellow, amorphous powder which does not part with the whole of its water at 150°. It is decomposed by acids into the

[1] Brislee, *Journ. Chem. Soc.*, 1908, **93**, 154.

[2] *Zeit. anorg. Chem.*, 1901, **27**, 304.

monoxide and dioxide, and is, therefore, considered to be a compound of these two, PbO,PbO_2, and may be termed *lead metaplumbate* (p. 890).

Red Lead or *Minium*, Pb_3O_4.—This compound was described by Pliny, under the name of *minium*, but it was at that time not sufficiently distinguished from cinnabar and the red sulphide of arsenic. Dioscorides, however, mentions that it can be prepared from white lead: "*cerussa, si coquatur rufescit*"; and Geber says: "*plumbum aduritur et fit minium.*"

Red lead is usually prepared by carefully heating very finely-divided pure massicot or white lead. For this purpose the oxide is heated for about twenty-four hours either on the flat hearth of a reverberatory furnace, or in barrel-shaped vessels open at both ends, the mass being frequently stirred and the heat not allowed to rise above dull redness (about 400°). The brightness and beauty of the colour depend much on the care spent on the roasting, as these properties are not wholly influenced by the absorption of oxygen, but more especially by the particular molecular condition of the material, and this is produced only at a given temperature.

Red lead is a scarlet, crystalline, granular powder, which, on heating, first assumes a finer red colour and afterwards turns violet, and lastly black, but on cooling regains its original tint. When more strongly heated, at about 470°,[1] it loses oxygen and is converted into the monoxide. Its specific gravity varies from 8·6 to 9·1. Commercial red lead frequently contains the yellow oxide, litharge, mixed with it, which may be extracted by repeatedly digesting with a solution of lead acetate. Red lead is largely used as a paint and also in the preparation of flint glass. For both of these purposes it is necessary that it should be as free as possible from iron, and in this case it is not infrequently prepared from white lead. Red lead is also adulterated with oxide of iron, red bole, powdered heavy spar, and brick dust. These substances remain undissolved when red lead is digested in warm dilute nitric acid to which a little sugar has been added, whilst the red lead is dissolved completely. Boiling hydrochloric acid extracts sesquioxide of iron from the impure oxide with formation of lead chloride and liberation of chlorine. Like the sesquioxide it is decomposed by acids into the monoxide or a corresponding salt, and the dioxide, and is therefore regarded as a compound of

[1] Milbauer, *Chem. Zeit.*, 1909, **33**, 950, 960.

two molecules of the former and one of the latter, $2PbO,PbO_2$, and may be termed *lead orthoplumbate* (p. 890).

Lead Dioxide, Lead Peroxide or *Puce-coloured Oxide of Lead*, PbO_2.—This substance was discovered by Scheele, who observed that red lead is coloured brown when treated with chlorine water, whilst Priestley found that nitric acid produces the same reaction. The properties of the puce-coloured lead oxide were more exactly examined by Proust and Vauquelin.

Lead dioxide may be prepared according to a variety of methods. The simplest plan is to act upon red lead with dilute nitric acid:

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

It is likewise obtained by the action of chlorine upon lead salts in the presence of alkalis (Wöhler), or by treating a hot solution of a pure lead salt with a soluble hypochlorite (Böttger):

$$PbO + NaClO = PbO_2 + NaCl.$$

It is also prepared by the electrolysis of a solution of sodium chloride, in which litharge is suspended.[1]

It is obtained in the dry way by fusing 4 parts of lead monoxide, 1 part of potassium chlorate, and 8 parts of nitre (Liebig and Wöhler). Lead oxide is also converted into the dioxide by the action of ozone as well as of hydrogen peroxide. It is deposited at the positive pole when a solution of a lead salt in nitric acid is decomposed by means of an electric current.[2]

This substance is found native in the form of plattnerite, which crystallises in black, hexagonal prisms having a specific gravity of 9·4. The artificial dioxide sometimes assumes the form of brownish-black, six-sided tablets, but generally consists of a dark brown powder having a specific gravity of 8·9 to 9·2.

Lead dioxide decomposes on heating into oxygen and the monoxide. It loses oxygen when simply exposed to sunlight, red lead being formed. It has a strongly oxidising action, and when triturated with one-sixth of its weight of sulphur, it takes fire and burns with a brilliant flame, forming sulphide of lead.[3] Aqueous hypophosphorous acid is at once oxidised with formation of lead phosphate. When exposed to sulphur dioxide at

[1] *Chemische Fabrik, Griesheim-Elektron,* German Patent, 124512.

[2] Wolman, *Zeit. Elektrochem.*, 1897, **3**, 537; Hollard, *Compt. rend.*, 1903, **136**, 229, and others.

[3] Vauquelin, *Ann. Chim. Phys.*, 1807, **62**, 221.

ordinary temperatures it becomes red-hot and is converted into lead sulphate, whilst nitrogen peroxide and even ammonia convert it into lead nitrate. A large number of organic acids and other carbon compounds when triturated with it likewise cause evolution of light and heat. When treated with aqueous hydrochloric acid, chloride of lead and free chlorine are formed.

Lead dioxide is often employed as an oxidising agent, as, for instance, in the analysis of organic substances containing sulphur, in order to separate the sulphur dioxide from carbon dioxide. The mixture of lead nitrate and dioxide obtained by treating red lead with nitric acid is employed under the name of oxidised red lead in the manufacture of lucifer matches.

Lead dioxide is capable of acting as a weak basic oxide, yielding the unstable tetravalent lead salts, and also as a peroxide and an acid-forming oxide, forming compounds to which the name *plumbates* has been given. *Orthoplumbates* having the composition $M^I_4PbO_4$ and *metaplumbates*, $M^I_2PbO_3$, are known,[1] and the free *metaplumbic acid*, $PbO(OH)_2$ or H_2PbO_3, is deposited at the positive pole as a black, lustrous substance on the electrolysis of a slightly alkaline solution of lead sodium tartrate.

The orthoplumbates of the alkaline earths are obtained by heating the carbonates or hydroxides with lead monoxide in presence of air, the *calcium* salt, Ca_2PbO_4, crystallising with four molecules of water in almost colourless, microscopic, transparent crystals. These compounds evolve oxygen on strongly heating, and it has been proposed to utilise this method for obtaining oxygen from the atmosphere on the large scale; the calcium salt has also been used as an oxidising agent.[2]

The hydrosol of hydrated lead peroxide (plumbic acid) has been prepared by the dialysis of potassium plumbate.[3]

Potassium Metaplumbate, $K_2PbO_3,2H_2O$, is obtained in crystals by fusing lead dioxide with excess of caustic potash in a silver crucible, dissolving in water and evaporating in a vacuum.[4] The solution gives with most metallic salts precipitates of the corresponding metaplumbates.

[1] Compare Bellucci, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 457.
[2] Kassner, *Arch. Pharm.*, 1890, **228**, 109; 1894, **232**, 375; 1895, **233**, 501.
[3] Bellucci and Parravano, *Atti R. Accad. Lincei*, 1906, [v], **15**, ii., 542.
[4] *Ann. Chim. Phys.*, 1844, [3], **12**, 490.

Calcium Metaplumbate, $CaPbO_3,4H_2O$, is obtained by digesting the orthoplumbate with sodium peroxide and water, and from this other metaplumbates have been obtained.[1]

As already mentioned lead sesquioxide and red lead may be regarded as the metaplumbate and orthoplumbate of lead, their constitution being represented by the formulæ $Pb^{II}PbO_3$ and $Pb_2^{II}PbO_4$. Lead metaplumbate has been prepared from the calcium salt and is identical with the sesquioxide.[2]

When calcium meta- or ortho-plumbate is heated in dry air at 250°, *calcium perplumbate*, $CaPb_2O_6$, is formed.[3]

Lead and the Halogens.

406 *Lead Fluoride*, PbF_2.—This compound is obtained by heating lead oxide or carbonate with hydrofluoric acid, or by precipitating a lead salt with a soluble fluoride. It is a white powder, almost insoluble in water and in hydrofluoric acid, but fairly soluble in hydrochloric and nitric acids. When treated with ammonia an easily soluble basic fluoride is formed. If a solution of lead chloride be precipitated with sodium fluoride the compound PbClF is formed. The formation of this compound has been confirmed by the thermal analysis of the system $PbCl_2$–PbF_2,[4] and a second compound, $PbCl_2,4PbF_2$, detected. The chloro-fluoride of lead (PbClF) is slightly soluble in water, dissolving without decomposition (Berzelius).

Lead Tetrafluoride, PbF_4.—This compound is probably formed by the action of strong sulphuric acid on the acid plumbifluoride, $3KF,HF,PbF_4$, but has not been obtained in the pure state. The foregoing double salt, which is isomorphous with the analogous tin derivative, is obtained by the action of hydrofluoric acid and potassium fluoride on lead tetracetate, or by fusing lead dioxide with potassium fluoride and treating the product with hydrofluoric acid. It forms monoclinic needles which evolve hydrogen fluoride at 230°, and at a higher temperature yield free fluorine.[5]

Lead Chloride, $PbCl_2$.—Dioscorides mentions that yellow oxide of lead when brought in contact with common salt and

[1] Grützner and Höhnel, *Arch. Pharm.*, 1895, **233**, 512.
[2] Höhnel, *Arch. Pharm.*, 1895, **233**, 501.
[3] Kassner, *Arch. Pharm.*, 1899, **237**, 409; 1900, **238**, 449.
[4] Sandonnini, *Atti R. Accad. Lincei*, 1911, [v], **20**, i., 172.
[5] Brauner, *Journ. Chem. Soc.*, 1894, **65**, 393.

warm water becomes white. After the discovery of silver chloride, to which the name of horn-silver was given, the corresponding lead compound was termed horn-lead (*plumbum corneum*). Lead chloride occurs native in the craters of volcanoes as the mineral cotunnite. Lead combines with chlorine, but slowly, and without incandescence. Dilute hydrochloric acid dissolves the metal only in the presence of air, and then but slowly. The boiling concentrated acid, however, converts it into chloride with evolution of hydrogen gas. Lead chloride is easily prepared by the action of hydrochloric acid on the oxide or carbonate, and also by the precipitation of a tolerably concentrated solution of a lead salt by means of hydrochloric acid or a soluble chloride. It is thus obtained in the form of a white, crystalline precipitate, of which 100 parts of water dissolve 0·909 part at 15°, and 3·2 parts at 100°. The salt crystallises, when a boiling solution is cooled, in white, silky, rhombic needles, having a specific gravity of 5·8. It is less soluble in dilute hydrochloric acid and solutions of chlorides than in pure water, but dissolves more freely in concentrated hydrochloric acid; hence a precipitate may be obtained by adding water to the latter solution, whilst the aqueous solution is precipitated by hydrochloric acid. It also dissolves readily in the solutions of the acetates and thiosulphates of the alkali metals. When heated in absence of air lead chloride melts at about 485°, solidifying on cooling to a white, translucent, horny mass; it volatilises at a temperature of 861–934°, the vapour having a density of 5·8, corresponding to the formula $PbCl_2$.[1]

Lead yields a large number of oxychlorides. The compound $PbCl_2,PbO$ occurs as the mineral matlockite, and may be obtained artificially by igniting the chloride in the air till no further fumes are evolved. The mineral mendipite has the composition $PbCl_2,2PbO$, and numerous others, some of which contain water of crystallisation, have been prepared. Ruer[2] has examined the freezing points of mixtures of lead oxide and lead chloride, and has obtained evidence of the existence of the compounds, $PbCl_2,PbO$, $PbCl_2,2PbO$, and $PbCl_2,4PbO$. The hydrate $PbCl_2,PbO,H_2O$, which may also be formulated as lead hydroxychloride, Pb(OH)Cl, and occurs as the mineral laurionite, was formerly prepared by a process patented by Pattinson in 1849.

[1] Roscoe, *Proc. Roy. Soc.*, 1878, **27**, 428.
[2] *Zeit. anorg. Chem.*, 1906, **49**, 365.

In this process chloride of lead is first prepared from finely pulverised galena and concentrated hydrochloric acid; this is then dissolved in water and mixed with lime-water in certain definite proportions; a snow-white precipitate having the composition given above is thrown down, which was at one time used as a paint in place of white lead.

A hydrated oxychloride is likewise obtained by warming lead oxide with a solution of common salt (Scheele), caustic soda being produced at the same time. In the year 1787 Turner took out a patent for the purpose of preparing caustic soda by this reaction, and found that the residue when heated became anhydrous and possessed a yellow colour. This oxychloride is known under the name of *Turner's yellow* or *patent yellow*. Vauquelin then showed that when lead chloride and lead oxide are fused together, a yellow-coloured body is obtained. This is now known as *Cassel yellow*, and is usually prepared by fusing together one part of ammonium chloride and about 10 parts of massicot, minium, or white lead; a part of the ammonium chloride sublimes undecomposed, and the resulting compound contains about one molecule of chloride to seven molecules of oxide, part of the lead being at the same time reduced by the ammonia.

Lead chloride also yields a number of double salts with the chlorides of other metals.

Lead Tetrachloride, $PbCl_4$.—A solution of this compound is obtained by dissolving the dioxide in well-cooled hydrochloric acid, but it is best prepared by passing chlorine into lead dichloride suspended in hydrochloric acid. On addition of ammonium chloride, *ammonium plumbichloride*, $(NH_4)_2PbCl_6$, crystallises out, and the same compound is also formed by acting on lead tetracetate with concentrated hydrochloric acid and then adding ammonium chloride.[1] It may also be obtained by the action of hydrochloric acid and ammonium persulphate on lead chloride in the cold,[2] or by the electrolysis of concentrated hydrochloric acid with lead electrodes, the cathode being placed in a porous pot, when an orange solution of H_2PbCl_6 is formed, and this on addition of ammonia yields the above compound.[3] When this compound is added to well-cooled sulphuric acid, it yields the tetrachloride, as a yellow, refractive,

[1] Hutchinson and Pollard, *Journ. Chem. Soc.*, 1896, **69**, 212.
[2] Seyewetz and Trawitz, *Compt. rend.*, 1903, **136**, 686.
[3] Elbs and Nübling, *Zeit. Elektrochem.*, 1903, **9**, 776.

fuming liquid, which readily decomposes into the dichloride and chlorine. It has a specific gravity of 3·18 at 0°, solidifies at −15° to a yellowish, crystalline mass, and yields a hydrate with a small quantity of water, but in presence of an excess is decomposed into lead dioxide and hydrochloric acid.[1]

Lead Bromide, $PbBr_2$.—This compound closely resembles the chloride. It is obtained by treating lead oxide with aqueous hydrobromic acid, or by precipitating a lead salt with a solution of potassium bromide, when it is thrown down in the form of white shining needles. It dissolves in hot water, and has a specific gravity of 6·6. When heated in a closed vessel it fuses, forming a red liquid which on cooling solidifies to a white horny mass. Fused in contact with the air it emits white fumes and leaves a residue of *oxybromide*, $PbBr_2,PbO$, forming a pearly yellow mass, whilst the *hydrated oxybromide*, $PbBr_2$, PbO,H_2O or PbBrOH, has been prepared by heating a mixture of solutions of sodium bromide and lead acetate.[2]

Lead Iodide, PbI_2.—Hydriodic acid easily dissolves lead, and the iodide separates out from a concentrated solution in beautiful yellow crystals (Deville). When a solution of lead salt is mixed with a soluble iodide a yellow precipitate of lead iodide is formed. This is soluble in 1,235 parts of cold and 194 parts of boiling water, giving rise to a colourless solution from which the iodide separates out on cooling in yellow laminæ resembling those of mosaic gold. The specific gravity of this compound is 6·1; on heating it becomes reddish-yellow, then bright red, and lastly brownish-black; it melts in a closed tube to a reddish-brown liquid which solidifies to a yellow, crystalline mass, and may be sublimed unchanged by heating in carbon dioxide.[3] Like the chloride and bromide, it easily forms basic salts.

A number of mixed halogen compounds of lead have been described, which are mostly prepared by the action of the halogen salts of potassium or ammonium on those of lead. In this way the compounds PbFBr, PbICl, and PbBrCl are stated to be formed, as well as double compounds of these with the halogen salts of ammonia.[4] There is, however, some doubt as to

[1] Friedrich, *Monatsh.*, 1893, **14**, 505; Classen, *Zeit. anorg. Chem.*, 1893, **4**, 100.

[2] de Schulten, *Bull. Soc. fran. Min.*, 1897, **20**, 186.

[3] Schtscherbakoff, *J. Russ. Phys. Chem. Soc.*, 1905, **37**, 682.

[4] Thomas, *Compt. rend.*, 1898, **126**, 1349; 1899, **128**, 1234, 1329; *Bull. Soc. chim.*, 1898, [3], **19**, 598; Fonzes-Diacon, *ibid.*, 1897, [3], **17**, 346.

whether these are true compounds or isomorphous mixtures of the halogen salts of lead.[1]

Lead and Sulphur.

407 *Lead Sulphide,* PbS, occurs in nature as galena, crystallised in cubes or in other combinations of the regular system. It possesses a bluish-grey colour, and has a specific gravity varying from 7·25 to 7·7. This mineral was known to the ancients under its present name, but the fact that it contained sulphur was not recognised until after some time. Thus even Kunkel was unacquainted with this fact, though Boyle[2] was aware that when galena is heated with scrap iron metallic lead is formed, and recommended this mode of producing lead.

When sulphur vapour is led over metallic lead it takes fire and burns, forming a crystalline sulphide, and even tolerably thick strips of lead take fire in sulphur vapour with a vivid glow, depositing half-fused globules of lead sulphide. It can also be prepared by fusing lead oxide with an excess of sulphur. When sulphuretted hydrogen is passed into a solution of lead nitrate, an amorphous, black precipitate is formed, but if the gas be passed into a dilute solution of the salt containing free nitric acid a crystalline precipitate is obtained, consisting of microscopic cubes (Muck).

Sulphide of lead fuses at a strong red heat—at $1120° \pm 10°$ according to Friedrich[3]—and when heated in a current of many gases sublimes in cubes which often have a diameter of 1·5 mm. Crystals of galena are often obtained in lead works in a similar way. On the other hand, octahedral crystals may be obtained by fusing one part of the precipitated sulphide with 6 parts of potash and 6 parts of sulphur (Schneider). Nitric acid converts galena, with separation of sulphur, partly into the nitrate and partly into the sulphate, the latter compound being formed in the largest quantity when the acid is strongest. Hot concentrated hydrochloric acid dissolves it with evolution of sulphuretted hydrogen.

When an aqueous solution of a lead salt containing an excess of hydrochloric acid is treated with a small quantity of sulphuretted hydrogen a yellowish- to dark-red precipitate is obtained, which

[1] Hertz and Bogg, *J. Amer. Chem. Soc.*, 1897, **19**, 820.

[2] A hydrostatical way of estimating ores of lead.

[3] *Metallurgie*, 1907, **4**, 479; 1908, **5**, 23.

consists of a double chloride and sulphide of lead. According to Hünenfeld,[1] this precipitate has the composition $3PbS,2PbCl_2$, whilst Parmentier[2] found the composition $PbS,PbCl_2$; it is converted by an excess of sulphuretted hydrogen into lead sulphide, and loses lead chloride on treatment with hot water. The compound $PbS,4PbCl_2$ has been obtained by diluting a solution of lead sulphide in concentrated hydrochloric acid, whilst similar compounds with lead bromide and iodide have also been prepared.[3]

A polysulphide of lead, PbS_5, is formed by the action of calcium polysulphide on lead nitrate at 0°, as a purple-red precipitate which decomposes rapidly at ordinary temperatures into the monosulphide and sulphur.[4]

Lead Sulphate, $PbSO_4$.—This substance is found native as lead vitriol or anglesite in transparent, rhombic crystals, isomorphous with those of celestine and heavy-spar, or as pseudomorphs of galena. It is obtained as a white powder by precipitating a lead salt with sulphuric acid or a soluble sulphate. If a layer of water be poured on to a saturated solution of potassium sulphate, and a platinum wire on which some lead chloride has been fused allowed to dip into the water, crystals of lead sulphate are gradually formed.[5] It may also be formed by the action of sulphur dioxide on lead peroxide.[6] Lead sulphate has a specific gravity of 6·2 to 6·3. It melts at about 1100° without decomposition. One part of the salt dissolves in 21,739 parts of cold water, 12,135 parts according to Schnal,[7] and in 36,504 parts of dilute sulphuric acid, whilst concentrated sulphuric acid can take up about 6 per cent. of the compound. It also dissolves in warm ammonia and caustic potash, and in hot hydrochloric acid with formation of lead chloride. Sulphate of lead is likewise very readily soluble in ammoniacal salts, especially in the acetate; calcium acetate and many other salts also dissolve it.

When lead sulphate is boiled with concentrated sulphuric acid, it is dissolved and is afterwards deposited in crystals, and if the mother-liquor be allowed to stand in contact with moist air

[1] *J. pr. Chem.*, 1836, **7**, 27.
[2] *Compt. rend.*, 1892, **114**, 299.
[3] Lenher, *J. Amer. Chem. Soc.*, 1895, **17**, 511; 1901, **23**, 680.
[4] Bodroux, *Compt. rend.*, 1900, **130**, 1397.
[5] Manross, *Annalen*, 1852, **82**, 360.
[6] Marino, *Zeit. anorg. Chem.*, 1907, **56**, 233.
[7] *Compt. rend.*, 1909, **148**, 1394.

crystals of the acid sulphate, $PbSO_4,H_2SO_4,H_2O$, similar to those of the corresponding barium salt, are formed.

When the normal salt is treated with ammonia the basic sulphate Pb_2SO_5 or $O<^{Pb\cdot O}_{Pb\cdot O}>SO_2$ is formed. The same salt is obtained in microscopic needles when an excess of a hot solution of sodium sulphate is added to basic lead formate (Barfoed). The basic sulphates, $PbSO_4,2PbO$ and $PbSO_4,3PbO$, also probably exist.[1]

Lead Persulphate, $Pb(SO_4)_2$, is obtained at the anode as a greenish-yellow, crystalline precipitate when a solution of sulphuric acid is electrolysed below 30° with an anode of lead placed in a porous pot. It is decomposed by water with formation of sulphuric acid and lead dioxide, and is a powerful oxidising agent.[2]

Lead and Nitrogen and Phosphorus.

408 *Lead Imide*, PbNH, is obtained by the action of potassamide on lead iodide in liquid ammonia, and is a reddish-brown explosive substance. If the lead iodide be in excess the white basic salt NPb_2I,NH_3 is obtained.[3]

Lead Nitrite, $Pb(NO_2)_2$.—This substance is most readily obtained by decomposing silver nitrite with lead chloride and concentrating the solution in a vacuum, when yellow prisms separate out, which are easily soluble in water. On evaporating the solution, nitric oxide is evolved, and a basic salt remains behind. If lead nitrate be digested with water in contact with finely-divided metallic lead for a few hours at a temperature of 75°, a yellow solution is formed, which on cooling deposits the basic double salt, $Pb(NO_3)OH$, $Pb(NO_2)OH$, in glittering yellow plates. Proust, who first obtained this compound, considered it to be a nitrate of a suboxide of lead, whilst Berzelius viewed it as a simple basic nitrite. If its solution be boiled with metallic lead and a large quantity of water, orange-yellow prisms separate out on cooling, having the composition $Pb(NO_2)_2,Pb(NO_3)_2,5PbO,3H_2O$. This salt was formerly termed *lead hyponitrate*. If lead nitrate be boiled with one and a half times its weight of lead, and fifty times its weight of water for twelve hours in a long-necked flask,

[1] Schenck and Rassbach, *Ber.*, 1908, **41**, 2917.

[2] Elbs and Fischer, *Zeit. Elektrochem.*, 1900, **7**, 343.

[3] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

pale red needles of basic nitrite of lead, $Pb(NO_2)_2,3PbO,H_2O$, are formed. Other basic nitrites of lead are known.[1]

Lead Nitrate $Pb(NO_3)_2$.—Lead nitrate is first mentioned in the *Alchymia* of Libavius. It is here termed *calx plumb. dulcis.* "Fit per aquam fortem comminuto plumbo affusam vase in aqua frigida locato. Fit instar crystallorum." Lead dissolves slowly in warm dilute nitric acid. Lead nitrate, or lead saltpetre as it is sometimes called, is prepared on the large scale by dissolving lead scale or litharge in hot dilute nitric acid, having a specific gravity of 1·35. The solution is evaporated until it attains a specific gravity of 1·6, and is then allowed to cool in earthenware vessels, when the salt separates out in milk-white regular octahedra exhibiting a combination of the regular dodecahedron. If a cold solution of the salt be allowed to undergo spontaneous evaporation, transparent octahedral crystals are formed (Knop). It has a specific gravity of 4·5, and on dissolving in water gives rise to a reduction of temperature; 100 parts of water dissolve, according to Mulder, as follows:

At	0°	10°	20°	40°	60°	80°	100°
$Pb(NO_3)_2$	36·5	44·4	52·3	69·4	88·0	107·6	127·0

It scarcely dissolves in strong alcohol and is only slightly soluble in aqueous alcohol. Its aqueous solution is precipitated by nitric acid. It has an astringent metallic taste, decrepitates when heated, detonates with brilliant sparks when thrown upon red-hot charcoal, and deflagrates when triturated with sulphur. When heated in a sealed tube at 357° it decomposes partially according to the equation:[2]

$$Pb(NO_3)_2 \rightleftharpoons PbO+O+2NO_2.$$

The salt is largely used in dyeing and calico-printing, for the preparation of mordants, and for the preparation of chrome-yellow.

When the normal salt is boiled with an equal weight of lead oxide and water, crystals of a basic nitrate, $Pb(NO_3)OH$, are thrown down on cooling. These are sparingly soluble in cold and more readily soluble in hot water. When gently heated it is converted into red lead. If a solution of the normal salt be precipitated with a slight excess of ammonia, and

[1] Compare Chitesotti, *Atti R. Accad. Lincei*, 1908, [v], **17**, ii., 377 and 474.

[2] Baekeland, *J. Amer. Chem. Soc.*, 1904, **26**, 391; Morgan, *J. Physical Chem.*, 1904, **8**, 416.

the solution heated in a closed vessel with the addition of some of the normal salt until the smell of ammonia has almost disappeared, a basic nitrate is formed, having the composition $2Pb(NO_3)OH,PbO$. It is a white powder slightly soluble in water. When an excess of ammonia is employed the compound $Pb(NO_3)OH,2PbO$ is thrown down as a white powder.

Phosphates of Lead.—When common sodium phosphate is precipitated by acetate of lead a white precipitate of normal lead orthophosphate, $Pb_3(PO_4)_2$, is formed. If a boiling solution of lead nitrate be precipitated by phosphoric acid, a glittering white crystalline precipitate of $HPbPO_4$ is produced, and the same compound is obtained in the form of crystalline needles when lead pyrophosphate is heated with water to 250°. The pyrophosphate and metaphosphate of lead are white precipitates.

The following minerals are lead phosphates and arsenates isomorphous with apatite:

Pyromorphite, $Pb_3(PO_4)_2,Pb_2Cl(PO_4)$,
Polysphærite, $(Pb,Ca)_3(PO_4)_2,(Pb,Ca)_2Cl(PO_4)$,
Mimetite, $Pb_3(AsO_4)_2,Pb_2Cl(AsO_4)$, and
Campylite, $Pb_3[(As,P)O_4]_2,Pb_2Cl[(As,P)O_4]$.

These usually contain a portion of their chlorine replaced by fluorine.

Borates of Lead.—If boron trioxide and lead oxide be fused together in the proportion of two molecules of the former to three of the latter, a yellowish soft glass is obtained, which softens when exposed to the action of hot oil. If double the weight of boron trioxide be employed the glass obtained is harder and less coloured, and if three times the weight be used a colourless glass is obtained, which possesses the hardness of flint glass and refracts light much more powerfully.[1] When a lead salt is precipitated with borax, a compound having the composition $Pb_2B_6O_{11},4H_2O$ is formed, and this when warmed with strong ammonia is converted into a heavy white powder having the composition PbB_2O_4,H_2O, which again, when boiled with a solution of boric acid, yields an amorphous powder of $PbB_4O_7,4H_2O$.

Lead and Carbon and Silicon.

409 *Carbonates of Lead.—Normal Lead Carbonate,* $PbCO_3$, occurs as cerussite or white carbonate of lead in rhombic crystals

[1] Faraday, "On the Manufacture of Optical Glass," *Phil. Trans.*, 1830, 120, 1.

isomorphous with aragonite, and also as pseudomorphs of galena and lead sulphate. The same compound is formed by precipitating a cold solution of lead acetate by ammonium carbonate (Berzelius), or by passing carbon dioxide into a dilute solution of lead acetate (Rose). Cerussite forms colourless, transparent, lustrous crystals, having a specific gravity of 6·46, whilst the precipitated carbonate has a specific gravity of 6·43. It is scarcely soluble in water, one part dissolving in 50,500 parts of water at the ordinary temperature, but in presence of ammoniacal salts it is somewhat more soluble (Fresenius). A solution of carbon dioxide in water also dissolves it slowly.

Lead forms several basic carbonates, among which *white lead* is the most important, since it is manufactured on a very large scale. In the pure state this compound consists of $2PbCO_3,Pb(OH)_2$, but the commercial product usually contains the normal carbonate in addition.

White Lead has long been known, being called ψιμύθιον by Theophrastus. The process of manufacture as described by him consisted in the action of vinegar on lead, the material formed being scraped off after a time from the surface of the metal. Pliny mentions the same subject under the name of *cerussa* and describes the above method of manufacture. He also states that it may be obtained by dissolving lead in vinegar and evaporating to dryness. Thus it would appear that the difference between white lead and sugar of lead was not known. The Latin Geber describes the manufacture as follows: "plumbum ponendo super vaporem aceti fit cerussa," a description which accords with the method employed even up to the present day. For some time white lead was supposed to be a compound of calx of lead with vinegar, and it was not until 1774 that Bergman showed that white lead contained lead calx and fixed air, and gave to it the name of "luftsaürer blei-kalk" or "calx plumbi ærata."

The oldest process for the manufacture of white lead is known as the *Dutch process*. In this method conical glazed earthenware pots, 8 inches wide, are filled to one-fourth of their depth with malt vinegar. At one-third of the height of the pot from the bottom are three projecting points on which a crosspiece of wood is laid, and on this are placed vertically a number of thin leaden plates rolled up into a spiral, and the whole covered with a leaden plate, which often has holes punched in it. The pots are then placed under a shed in rows upon horse dung or spent

tannery bark and covered with boards; another layer of dung or decomposing bark is laid upon the boards, and on this another row of pots, many rows of pots being thus placed above one another, and the whole covered by the tan or dung. By the slow oxidation of the dung heat is evolved, which assists the evaporation of the vinegar and causes basic lead acetate to be formed, and this in contact with the carbon dioxide evolved from the putrefaction of the organic matter is converted into white lead. In the course of from four to five weeks the greater portion of the lead is converted into white lead, the change taking place from without inwards. The white lead is then detached, ground into a fine paste whilst moist, washed well to free it from adhering acetate, and dried in small round pots. Unwashed white lead contains a considerable quantity (from 2 to 12 per cent.) of the normal acetate.

To reduce the risk of poisoning attending the drying of the white lead pulp, formed by the treatment of the corroded lead with water, it is customary in some works to dry the pulp in ovens in which a vacuum is maintained. A further improvement, applicable in the manufacture of paint, is that described by Ismay (English Patent 23969, 1895) in which the white lead pulp is mixed with oil in a pug mill; in this way the greater portion of the water is displaced by the oil, and the last portion is driven off from the paint by surrounding the mill with a heating jacket so arranged that the contents are heated in a partial vacuum. In this way the use of drying stoves and the dangers attending it are completely obviated.

According to the *German method* of manufacture, plates of lead are hung up in wooden boxes placed in an atmosphere of carbon dioxide in heated chambers containing a stratum of acetic acid, or the plates are suspended in heated chambers having their floors covered with tan and acetic acid.

The *French method,* introduced by Thénard, and the *English method,* suggested by Benson, do not furnish a white lead which possesses the same covering power as that prepared by the other methods. The process in these cases consists in passing carbon dioxide through a solution of a basic acetate of lead, obtained by boiling a solution of lead acetate with litharge.

Another method, which yields a white lead of excellent covering power, is the process patented by Dale and Milner. This consists in carefully grinding between millstones a mixture of litharge, or any insoluble basic lead salt, with water and

sodium bicarbonate. Milner has improved upon this method by grinding a mixture of 4 parts of finely-divided litharge with 1 part of common salt and 16 parts of water. After about 4½ hours the reaction is complete. The mixture of basic lead chloride and caustic soda is then brought into a leaden vessel, well stirred with a wooden pestle and a current of carbon dioxide passed through it until the liquid is neutral. If the carbon dioxide be passed in too long the product is spoiled.[1]

Another process, called, after its discoverer, the *Bischof process*, is now employed on a large scale at Mond's works at Brimsdown in Middlesex.[2] Metallic lead is converted into litharge, and the latter is heated at 250–300° in a stream of water gas. It is thereby reduced to a black suboxide of unknown composition, and this is treated with water, when a yellow hydrate is formed with evolution of heat, which is further converted into white lead by treatment with carbon dioxide. This process, besides being rapidly completed, has the advantage of being carried out mechanically, and in such a manner that there is no dust, and thus a great source of danger to the workers is avoided. The product has a composition practically identical with that formed by the German process.

Several electrolytic processes have been proposed, but only a very small amount of white lead is produced by this means.[3]

White lead is a white, earthy, heavy, amorphous powder which appears under the microscope to consist of round transparent globules of the size of from 0·00001 to 0·00004 of an inch in diameter. The specific gravity of that prepared by the Dutch method is somewhat greater than that prepared by the French method, and it therefore absorbs less oil or varnish and gives rise to a thicker colour.

Although it acts as a powerful poison, and is turned black by sulphuretted hydrogen, white lead is still almost exclusively used as the basis of paint, and has been replaced only to a very small extent by zinc-white or baryta-white. This is accounted for by the fact that it possesses a much greater covering power and is much more opaque than either of the other two.

White lead is often mixed with heavy-spar and gypsum. A mixture of equal parts of white lead and barium sulphate is

[1] Patent No. 4,053; 22nd November, 1875.

[2] Caro, *Verh. des Vereins zur Beförderung des Gewerbfleisses, Berlin*, 1906.

[3] Luckow, D. R. P., 91707 and 105143; Browne and Chaplin U. S. P., 1895, 551361 and 1896, 555232.

known as *Venetian white*, whilst *Hamburg white* is a mixture of one part of white lead to two of barium sulphate, and *Dutch white* of one part to three of barium sulphate. The amount of this admixture may be readily ascertained by treating a weighed portion of the powder with warm dilute nitric acid, when the barium sulphate remains behind.

Lead Cyanide, $Pb(CN)_2$, is obtained as a white powder when a solution of a normal lead salt is mixed with potassium cyanide. It is not soluble in the cyanides of the alkali metals and is decomposed on the addition of an acid. When heated in a closed vessel a mixture of lead and charcoal remains behind which, if it has not been too strongly heated, is pyrophoric.

Lead Cyanate, $Pb(CNO)_2$, is obtained by mixing solutions of a cyanate and of a soluble lead salt. A dense white precipitate is thrown down, which soon assumes the form of slender needles like chloride of lead. Under the action of boiling water lead cyanate is readily and quantitatively hydrolysed into lead carbonate and urea.[1]

Silicates of Lead.—Silica fuses with lead oxide to form a yellow glass, and silicates obtained by "fritting" lead oxide with silicious material are used by potters for preparing glazes. Glass formed of equal parts of lead oxide and silica does not become dull when it is exposed to the action of sulphuretted hydrogen, but if 8 parts of the glass are fused with one part of potash, the glass produced becomes tarnished on exposure.[2] In a similar manner it has been found by Thorpe and Simmonds[3] that the extent to which lead silicates are attacked by dilute hydrochloric acid depends upon the proportion of acidic to basic oxides present. When there are present in the silicate two or more molecules of acidic oxides to one of basic oxide, dilute acid dissolves out very little lead, whereas when this proportion falls below two, the silicates are readily attacked. Lead silicate forms a constituent of flint glass. The existence of the definite compounds $2PbO,SiO_2$ and PbO,SiO_2 has been proved by various methods of investigation, and the existence of the compound $3PbO,2SiO_2$ is probable.[4]

[1] Cumming, *Journ. Chem. Soc.*, 1903, **83**, 1391.

[2] Faraday, "On the Manufacture of Optical Glass," *Phil. Trans.*, 1830, **120**, 1.

[3] *Journ. Chem. Soc.*, 1901, **79**, 791.

[4] Hilpert and Weiller, *Ber.*, 1909, **42**, 2969; Cooper, Shaw & Loomis, *ibid.*, 3991; Hilpert and Nacker, *ibid.*, 1910, **43**, 2565; Cooper, Kraus & Klein, *Amer. Chem. J.*, 1912, **47**, 273.

Poisonous Action of Lead Salts.

410 The soluble lead salts are strongly poisonous and are employed in medicine. The normal or basic acetate given in doses containing 1 to 4 grams of lead mostly produces symptoms of acute lead poisoning, whilst 10 grams is said to be a fatal dose.

When taken for a considerable time in small doses, especially in the case of the oxides and carbonates, chronic lead poisoning is observed. The disease called painters' colic is the chronic form of poisoning by carbonate of lead. The symptoms are pain in the abdomen, constipation, loss of appetite, thirst, and general emaciation, followed by a complex of nervous symptoms known as lead-palsy, epileptic fits, and total paralysis.

A very characteristic phenomenon accompanying chronic lead poisoning is the appearance of a blue line at the edges of the gums due to the deposition of lead sulphide. This line is often seen in the case of house-painters and the workmen engaged in white lead works, as well as those occupied in manufactures in which white lead is employed, as, for instance, in the manufacture of glazed cards. Plumbers and others who have to handle metallic lead are also subject to lead poisoning.

A serious source of lead poisoning is the material used by potters for compounding their glazes. This generally consists of litharge, white lead, and red lead, which are readily dissolved by the acids of the gastric juice, and the use of suitable lead silicates has been suggested in place of these substances.[1]

The Action of Water upon Lead.

411 Since lead acts as a cumulative poison, its salts produce serious results if taken into the system even in very minute quantities for a length of time. Drinking water is often collected in lead-lined cisterns and passes through leaden pipes, and as water in certain circumstances can take up notable quantities of lead it becomes of great importance to determine the conditions under which the solvent action is exerted. A fresh bright surface of lead does not tarnish in a perfectly dry atmosphere nor when sealed up in a vessel filled with pure distilled water from which all air has been expelled by boiling.

[1] Thorpe and Simmonds, *Journ. Chem. Soc.*, 1901, **79**, 791.

If, however, it be exposed to the united action of air and water the lead is oxidised to hydroxide, which dissolves. After a time, this is converted by the action of the atmospheric carbon dioxide into an insoluble basic carbonate. Lead hydroxide is then again formed, and thus the corrosive action may be continued.

Potable waters always contain a certain amount of salts in solution and the corrosive action on lead depends upon the nature and quantity of the salts thus present. The ammoniacal salts act most prejudicially on water in this respect; this is especially the case with ammonium nitrate, which greatly assists the oxidation and solution of the lead. Other nitrates do not, however, appear to possess this power, and sulphates, phosphates, carbonates, and silicates either retard or altogether prevent this action, and hence water containing carbonic acid in solution or temporarily hard water consisting of a solution of calcium carbonate in carbonic acid gives rise to the formation of insoluble basic lead carbonate[1]; if, however, an excess of carbon dioxide be present, this is dissolved, the water taking up lead in considerable quantity.

The following table (p. 906) contains the results of experiments on the solubility of lead in water containing various salts in solution. Bright plates of lead having a surface of 5,600 sq. mm. were placed in flasks containing 500 c.c. of water in which the salts were dissolved, and the saline solutions allowed to act upon the lead for different periods of time.[2]

Many potable waters act as a solvent of lead, especially waters of a peaty nature which contain organic acids (ulmic and humic acids) and waters containing little or no free carbonic acid, and destitute of calcium and magnesium salts. Occasionally otherwise pure waters are found to contain a trace of free sulphuric acid sufficient to render the water plumbo-solvent and liable to cause lead poisoning.

Epidemics of lead poisoning from such sources have necessitated the treatment of the water by the addition of calcium carbonate (precipitated chalk) alone, if such water contains sufficient free carbonic acid to enable 1·5 grains $CaCO_3$ per gallon to be dissolved, or if the water will not

[1] See also Antony and Benelli, *Gazz.*, 1896, **26**, ii., 97; 1898, **28**, ii., 135.

[2] Muir, *Proc. Manch. Phil. Soc.*, 1875, **15**, 31; *Journ. Chem. Soc.*, 1877, i., 660. See also Carnelley and Frew, *J. Soc. Chem. Ind.*, 1888, **7**, 15, 78; Reichardt, *Arch. Pharm.*, 1887, [3], **25**, 858, 1059; Müller, *J. pr. Chem.*, 1887, [2], **36**, 317.

dissolve this amount, the addition of from 1 to 5 grains of sodium carbonate (Na_2CO_3) per gallon also.

Salt.	Grams per Litre.	Milligrams per Litre of Lead dissolved.		
		24 hours	48 hours.	72 hours.
NH_4NO_3	0·02	13·0	—	25·0
"	0·04	15·0	—	32·0
KNO_3	0·02	2·0	2·0	—
$NaNO_3$	0·05			
KNO_3	0·07	—	—	0·5
K_2SO_4	0·50			
KNO_3	0·045	—	—	0·3
K_2CO_3	0·308			
$CaCl_2$	0·25	0·5	0·5	0·5
NH_4NO_3	0·02	—	—	1·8
$CaCl_2$	0·06			
Na_2SO_4	0·02			
K_2CO_3	0·04	—	—	0·1
$CaCl_2$	1·10			
K_2CO_3	0·31	—	—	0·2
Distilled water with carbon dioxide at ordinary pressure		3·0	—	3·0
Ditto with carbon dioxide at a pressure of about 6 atmospheres		14·8	24·0	—
Distilled water		2·0	2·0	3·0

In testing for the presence of lead in water it is important to avoid any form of filtration inasmuch as lead salts mordant with the filtering paper, and only a small amount of the original soluble lead is found in the filtrate.

Detection and Estimation of Lead.

412 The soluble lead salts possess a sweet astringent taste, whence the name "sugar of lead" has been given to the acetate, and are very poisonous. These two properties of the lead compounds have been long known, and it became in early times of importance to detect the presence of lead, inasmuch as the com-

pounds of this metal were largely employed for a great variety of purposes. Thus, for instance, the Romans were in the habit of boiling their poor wines in leaden vessels, and Pliny mentions the fact that the point at which the wine becomes sour can be detected by hanging a strip of lead in it and then observing when this undergoes any change in its appearance. In later times the addition of metallic lead to a cask of sour wine was said to render it drinkable. At a still later date, litharge appears to have been employed for the same purpose. It was observed that the treatment of wine with lead could be detected by the addition of sulphuric acid, and in 1707 Zeller suggested that an extract of orpiment and lime water (containing, therefore, sulphide of calcium) was an invaluable test for the presence of lead, inasmuch as this liquid turns all lead salts black. This reaction led to the simultaneous suggestion, in 1787, by Fourcroy and Hahnemann, of the application of water acidified with hydrochloric acid and then saturated with sulphuretted hydrogen for the detection of lead, and thus the most important reagent which we now employ in analytical chemistry for the detection and separation of the metals was introduced.

Potable water may be examined in this way for lead by passing sulphuretted hydrogen through water slightly acidified with hydrochloric acid. It is, however, to be remembered that many other metals, such as mercury, copper, and bismuth, also produce black precipitates. The absence of these metals must, therefore, be ascertained before the presence of lead can be certainly proved. Black lead sulphide can be readily distinguished from other black sulphides insoluble in dilute hydrochloric acid by dissolving it in warm dilute nitric acid and filtering the solution; on addition of sulphuric acid to the filtrate, from which the excess of acid should be removed by evaporation, a white precipitate of lead sulphate is obtained. By means of this reaction lead may be detected in the presence of all the other metals and separated from them. Lead compounds, heated before the blowpipe on charcoal, yield a malleable bead of lead readily soluble in warm nitric acid, and the solution yields a precipitate with sulphuric acid.

Another characteristic test for lead is, that when present in not too dilute solution, a crystalline precipitate of the chloride is obtained on the addition of hydrochloric acid. This is soluble in boiling water, and separates out on cooling in crystalline needles. Potassium chromate gives, in the presence of free

nitric acid, a fine yellow precipitate of chrome yellow, $PbCrO_4$. In order to detect small quantities of lead in presence of large masses of organic matter, as is necessary in cases of lead poisoning, the mass is evaporated to dryness, with sodium carbonate, the residue ignited gently, and the carbonised mass rubbed fine and carefully lixiviated, when small glittering heavy spiculæ of metallic lead remain behind. These can be examined as already described.

Lead is easily estimated gravimetrically in the form of sulphate, being precipitated by adding dilute sulphuric acid and then two volumes of absolute alcohol. For certain separations lead is also estimated as the chloride. In this case the solution is precipitated by hydrochloric acid, evaporated on a water-bath and the concentrated liquid treated with a mixture of ether and alcohol, in which the chloride is insoluble. Lead carbonate and lead oxalate are also occasionally used for the estimation of lead, and these precipitates are then converted by ignition into lead oxide.

Volumetrically, lead is generally determined by the titration of the solution of lead sulphate in ammonium acetate solution with a standard solution of ammonium molybdate, the end point being detected on a spot plate by means of tannin solution.

Lead is also estimated electrolytically. When a solution of lead salt to which 5 to 7 per cent. of nitric acid has been added is electrolysed, lead peroxide is deposited at the anode.

Lead compounds impart a pale tint to the non-luminous gas-flame and this exhibits characteristic lines in the green (Werther). The spark spectrum of lead contains a large number of lines between the orange and violet. The brightest and most characteristic of these are a violet line (4058), a somewhat less bright one in the green (5608), and a fainter one lying near the less refrangible of the "D" lines of Fraunhofer (5875) (Lecoq de Boisbaudran).

The Atomic Weight of lead was determined by Berzelius,[1] by the reduction of pure lead oxide in hydrogen, his results giving the number 207·06; later,[2] during his experimental work on the determination of the atomic weight of sulphur, he converted lead first into nitrate and then into sulphate, and from his results the number 206·96 is obtained. Turner[3] by a similar

[1] *Lehrbuch*, **3**, 1218. [2] *Lehrbuch*, 5th ed., **3**, 1187.
[3] *Phil. Trans.*, 1833, **123**, 527.

method obtained 207·04, and Stas [4] 206·92. Baxter and Wilson [5] have more recently determined the atomic weight by analyses of lead chloride which had been previously fused in an atmosphere of hydrogen chloride; from the ratio of lead chloride to silver, the number 207·088 is obtained, and from the ratio to silver chloride, 207·096 is obtained. The number now (1913) adopted is 207·1.

[4] *Bull. Acad. roy. Belg.*, 1860, [2], **10**, 298.
[5] *J. Amer. Chem. Soc.*, 1907, **30**, 187.

GROUP V.

Sub-group (a).	*Sub-group (b).*
Nitrogen.	Phosphorus.
Vanadium.	Arsenic.
Columbium (Niobium).	Antimony.
Tantalum.	Bismuth.

413 As in the preceding group (p. 804), the members of the two sub-groups resemble one another, especially in chemical properties, very closely, although they differ in certain respects.

All the elements of the group are characterised by the existence of acid-forming oxides of the empirical formula R_2O_5, the acidity of the resulting acid diminishing as the atomic weight of the element rises. Thus it is doubtful whether any salts of bismuthic acid exist, whereas the vanadates, arsenates, &c., are well-defined and stable salts.

The three elements, vanadium, columbium, and tantalum, which, together with nitrogen, belong to the even series, combine so readily with oxygen that it is extremely difficult to obtain them in the free state. They all have a metallic appearance, and melt and boil only at very high temperatures. They moreover do not form volatile compounds with hydrogen or the alcohol radicals.

The elements of the odd series, phosphorus, arsenic, antimony, and bismuth, on the other hand, are easily reduced from their oxides, melt at moderate temperatures, and can all readily be volatilised. They exhibit in their external characteristics the gradual passage from a well-marked non-metallic element (phosphorus) to a well-defined metal (bismuth), and the same progression is to be traced also in their chemical properties. Thus the lower oxide of phosphorus, of the empirical formula P_2O_3, is the anhydride of a well-marked acid, but does not yield salts, even with strong acids. Arsenious oxide yields unstable salts with strong acids, such as sulphuric acid; the corresponding oxide of antimony yields more stable salts, and the trioxide of bismuth is entirely devoid of acid-forming properties, and reacts with acids to form a whole series of salts of the type RX^I_3. The same increase in basicity is observable in the sulphides of

these elements, and, as already remarked, in the case of the pentoxides.

Phosphorus, arsenic, and antimony, as well as nitrogen, yield very characteristic volatile hydrogen compounds, but no analogous derivative of bismuth has yet been prepared. They all, however, form organo-metallic derivatives.

The group is further characterised by the large number of oxides and halogen derivatives formed by its members. In many of these the valency of the elements varies considerably. They are all distinguished by a tendency to form two series of compounds of the types RX^{I}_{3} and RX^{I}_{5} (or $R_2X^{II}_{3}$, $R_2X^{II}_{5}$), but, in addition to this, some of them act also as dyads and tetrads. Thus nitrogen is divalent in nitric oxide, NO, and tetravalent in nitrogen peroxide, NO_2, whilst vanadium forms a dichloride, VCl_2, and a tetrachloride, VCl_4.

The elements, nitrogen, phosphorus, and arsenic, and their chief derivatives, have already been described in Vol. I.

THE VANADIUM GROUP.

VANADIUM. V = 51·0.

414 In 1801, Del Rio pointed out the existence of a new metal in a lead ore found at Zimapan, in Mexico,[1] and gave to it the name Erythronium, from the fact that its salts became red when heated with acids. In 1805, Collet-Descotils[2] expressed his opinion that this supposed new metal was an impure oxide of chromium, and Del Rio accepted this conclusion as correct. In 1830, Sefström[3] described a new metal which he found in the celebrated iron of Taberg, and for this he proposed the name of Vanadium, from *Vanadis*, a cognomen of the Scandinavian goddess Freia. In the same year Wöhler[4] showed that Del Rio's discovery was a true one, and that the Zimapan ore was a vanadate of lead. Unable to carry out the further investigation of the new metal, Sefström handed the materials, amounting only to a few grams, to Berzelius, and in 1831 this chemist[5] published the results of an exhaustive investigation on the subject, in which he described a large number of vanadium compounds, and came to the conclusion that vanadium

[1] *Gilbert's Ann.*, 1801, **71**, 7.
[2] *Ann. Chim. Phys.*, 1805, [1], **53**, 260.
[3] *Pogg. Ann.*, 1830, **21**, 48.
[4] *Pogg. Ann.*, 1831, **22**, 1.
[5] *Pogg. Ann.*, 1831, **22**, 1.

closely resembled chromium and molybdenum, yielding, like these metals, an acid-forming trioxide. This view was universally adopted until the year 1867, when Roscoe showed that the substance supposed by Berzelius to be vanadium was, according to the mode of its preparation, either an oxide, or a nitride; that the volatile trichloride of Berzelius contained oxygen and possessed a composition analogous to that of phosphorus oxychloride; and that the metal, instead of belonging, as was supposed, to the chromium group, was a member of the antimony group and intimately connected with the nitrogen phosphorus, and arsenic family.[1]

415 Vanadium is a somewhat rare substance, forming an essential constituent of only comparatively few scarce minerals. Traces of this element, are, however, tolerably widely distributed throughout terrestrial matter; it is found in meteorites of the stony type,[2] and it exists in the sun.

The principal vanadium minerals are vanadinite, or lead vanadate, $3Pb_3(VO_4)_2,PbCl_2$; dechenite, $(Pb,Zn)(VO_3)_2$; descloizite, $Pb_2V_2O_7$; pucherite, $BiVO_4$; psittacinite, $(Pb,Cu)_3(VO_4)_2$, $3Cu(OH)_2,6H_2O$; volborthite, $(Cu,Ca)_3(VO_4)_2,H_2O$; roscoelite (vanadium mica) a vanadium muscovite, containing the metal as the basic oxide[3] V_2O_3; mottramite, $(Pb,Cu)_3(VO_4)_2,2(Pb,Cu)$

[1] A bibliography has been compiled by Prandtl (Liepzig, 1906, Voss). More complete information concerning the compounds of vanadium may be obtained from the monograph by Ephraim (Stuttgart, Enke, 1904).

[2] Hasselberg, *K. Vet. Akad. Förh. Stockholm*, 1899, **56**, 131.

[3] Hillebrand, Turner and Clarke, *Amer. J. Sci.*, 1899, [4], **7**, 451. It occurs in fairly large quantities associated with gold and gold tellurides in Eldorado Co. in California; also in Colorado and at Kalgoorlie in Western Australia. The following are the analyses of roscoelite from I. Granite Creek, Eldorado Co., California, and II. Placerville, Colorado:—

	I.	II.
SiO_2	45·17	46·06
TiO_2	0·78	—
V_2O_3	24·01	12·84
Al_2O_3	11·54	22·55
Fe_2O_3	—	0·73
FeO	1·60	—
CaO	—	0·44
BaO	—	1·35
MgO	1·64	0·92
K_2O	10·37	8·84
Na_2O	0·06	0·22
H_2O (105°)	0·40	1·98
H_2O (above 105°)	4·29	4·07
	99·86	100·00

$(OH)_2$; sulvanite, $3Cu_2S,V_2S_5$; carnotite, a potassium uranium vanadate found in Colorado; and patronite, an impure sulphide of vanadium, which occurs in considerable quantity in Peru. Mottramite has been found in tolerable quantity in the copper-bearing beds of the keuper, worked at Alderley Edge and Mottram St. Andrews in Cheshire, and it is from this source that the vanadic acid of commerce was at one time obtained, it having been for some time manufactured on the large scale by the Magnesium Metal Company at Patricroft near Manchester. Small amounts of vanadium have also been found in a large number of clays, in trap and basalt,[1] in certain iron ores, especially magnetite,[2] and cast-iron, in larger quantities in the slag from the basic steel process at Creuzot, in rutile, in the ash of trees, in certain coals, lignites, and peats, and also in soda-ash, as well as in sodium phosphate.

Extraction and Preparation of the Vanadium Compounds.—The methods adopted for the preparation of vanadium compounds from their various sources depend upon the discovery by Sefström of an insoluble ammonium metavanadate, which by repeated crystallisation can be obtained free from phosphorus and other impurities.

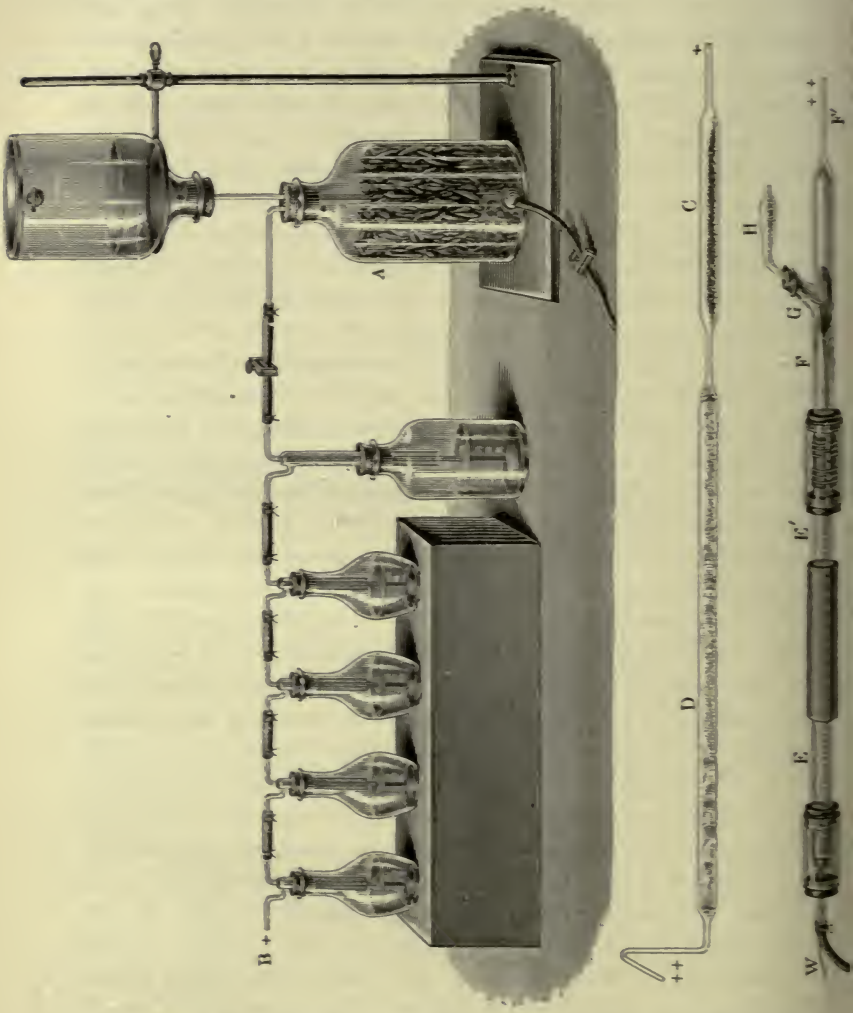
In order to prepare vanadium salts from mottramite, the keuper-sandstone, which contains the mineral deposited as a film on the surface of the grains of sand, is digested with strong hydrochloric acid, the acid liquor drawn off and the sand well washed with water. The acid solution, together with the washings, is evaporated down with an excess of ammonium chloride, when ammonium metavanadate separates out, and this is repeatedly crystallised to free it from copper and iron. The crude ammonium metavanadate is then gently roasted in porcelain, by which means the vanadium pentoxide is obtained in a tolerably pure condition. In order to purify this it is suspended in water and ammonia gas passed into the liquid. A solution of ammonium vanadate is thus formed, which is separated by filtration from the residue containing silica, phosphates, &c., and then crystallised by evaporation in platinum vessels; the pentoxide obtained by several repetitions of this treatment is free from phosphorus.

416 *Metallic Vanadium.*—Berzelius obtained brilliant metallic scales by heating the oxytrichloride in an atmosphere of ammo-

[1] See Hillebrand, *Amer. J. Sci.*, 1898, (4), **6**, 209; **7**, 294.

[2] See Pope, *Journ. Chem. Soc.*, 1900, **78**, ii. 409.

nia. These do not, however, consist of metallic vanadium, but of vanadium nitride. Pure metallic vanadium was first obtained by the reduction of the dichloride in perfectly pure hydrogen. Although this process appears simple enough, there is no metal



more difficult to prepare in this way than vanadium. This arises from the fact that whilst vanadium is stable at the ordinary atmospheric temperatures, it absorbs oxygen at a red heat with the greatest avidity, so that every trace of air or moisture must be excluded during its preparation. Moreover, the dichloride itself cannot be readily obtained in quantity.

For the purpose of reducing the chloride the apparatus shown in Fig. 184 is employed. It consists of a hydrogen generator (A) yielding a stream of hydrogen which can be kept constantly passing through the wash-bottles, day and night for a week at a time, by occasionally adding fresh acid to the upper bottle and drawing off the zinc sulphate solution from the lower bottle by the caoutchouc tubing. The first wash-bottle contains a solution of lead acetate, the second one of silver nitrate, and the three others contain boiled sulphuric acid. In order to remove any trace of oxygen which may have accompanied the hydrogen, arising either from diffusion or from air absorbed in the dilute acid used, a tube (CD) is attached to the last washing-bottle; the first portion of this tube contains a quantity of platinum sponge (C) which is heated to redness during the whole time the hydrogen is passing through the apparatus, whilst the further portion of the tube (D) is filled with phosphorus pentoxide and plugs of cotton-wool. The greatest care must be taken to have all caoutchouc stoppers and joints made as tight as possible with copper-wire and paraffin. At right angles to the drying tube (CD) is placed the reducing arrangement shown in the lower part of the drawing. This consists of a porcelain tube (EE′) placed in a Hofmann's furnace and protected in the central portions, where it is heated by an outer casing of sheet-iron. The porcelain tube is connected with the hydrogen apparatus by means of the wide glass tube (FF′) provided with the tubulus (G) and narrowed down to join the drying tube at F′. The joint between the porcelain and glass tubes is made of seamless caoutchouc, well wired and covered by an outer short glass cylinder, the space between the tubes and the cylinder being filled either with mercury or fused paraffin, and a similar joint is placed at the further end of the porcelain tube.

The introduction of the anhydrous dichloride without exposure to the air is effected by means of the tubulus (G), the dichloride being contained in the bent tube (H) in which it was prepared and sealed up in hydrogen. After the whole arrangement has been set up, the platinum boat being in position, as shown in the figure, hydrogen is allowed to pass through the apparatus for twelve hours to dry it completely and clear out the air; the caoutchouc stopper of the tubulus is then withdrawn and the end of the tube containing the dichloride cut off, and the tube and stopper quickly replaced, so that the crystals lie in the

horizontal portion of the tube. The bent tube is next so turned in the stopper that the crystals of dichloride fall out and are collected in the platinum boat placed below. This boat, charged with dichloride, is then drawn into the centre of the porcelain tube by means of the platinum wire, the end of which (w) passes tightly through a small hole in the caoutchouc tube at the end of the apparatus. As soon as the boat is in position the wire is cut off short at the end of the glass tube, a proper joint made, and an exit tube attached dipping under sulphuric acid.

Before the porcelain tube is heated, the caoutchouc stopper of the tubulus is surrounded by a bath of paraffin and the hydrogen is allowed to bubble through for six hours. The temperature of the porcelain tube is then gradually raised to the highest point (a bright red heat), which the Hofmann's furnace will yield, and kept constant until the reduction is complete. Torrents of hydrogen chloride at once come off, and the process must be continued for some hours after the last trace of acid can be detected in the hydrogen. The process lasts from forty to eighty hours, according as the quantity of dichloride employed varies from 1 to 3 or 4 grams.

Attempts to prepare vanadium on a somewhat larger scale were not at first successful. Thus reduction of the pentoxide with carbon in the electric furnace yielded only an impure metal, containing a large amount of carbon.[1] It has, however, been found that pure vanadium can be prepared by reducing the pentoxide with a mixture of the metals of the rare earths, known as "mischmetall," obtained by the reduction of the waste oxides from the manufacture of thoria.[2] The oxide is mixed with the finely divided metal in a magnesia crucible and the mass ignited, as in the aluminium thermite process; a violent reaction occurs and a regulus of pure vanadium is produced.

A regulus of crude vanadium, probably consisting of a mixture of the metal and the dioxide, can be obtained from vanadic oxide by Goldschmidt's aluminium reduction method. It can be used for the preparation of the tetrachloride.[3]

The metal has been prepared also by passing the electric current through thin rods of V_2O_3 contained in a vacuum,[4]

[1] Moissan, *Compt. rend.*, 1893, **116**, 1225.
[2] Weiss and Aichel, *Annalen*, 1904, **337**, 380.
[3] Koppel and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 352.
[4] Werner von Bolton, *Zeit. Elektrochem.*, 1905, **11**, 45.

and by heating the trioxide and carbide in a zirconia crucible to 1950°.[1]

Metallic vanadium prepared by reduction from the dichloride in hydrogen, is a light whitish-grey coloured powder, which under the microscope reflects light most powerfully, and appears as a brilliant crystalline metallic mass possessing a silver-white lustre. The surface of a regulus of the metal is covered with twinned rhombohedral crystals, and the metal has a hardness greater than that of steel or quartz. It is of a brilliant silver-white colour and takes a splendid polish, which is not affected by air. Vanadium does not decompose water at the ordinary temperature and it may be moistened and again dried in a vacuum several times without gaining in weight. Vanadium is neither volatile nor fusible when heated to redness in hydrogen. When the powdered metal is thrown into a flame, or rapidly heated in an excess of oxygen, it burns with brilliant scintillations. The specific gravity of vanadium at 15° is 5·5, and the atomic heat, as deduced from the specific heat of its alloys, is normal.[2] The metal is not attacked by hydrochloric acid either when cold or hot, and neither strong nor dilute sulphuric acid acts upon it in the cold, but when heated with the strong acid it slowly dissolves, giving a greenish-yellow solution. Hydrofluoric acid dissolves the metal slowly with evolution of hydrogen and formation of a green solution, whilst nitric acid of all strengths oxidises it with violence, evolving nitrous fumes and forming a blue liquid. Vanadium also dissolves readily in chloric acid, perchloric acid, and ammonium persulphate, vanadic acid being produced.[3] Both hot and cold solutions of caustic soda are without action on the metal, but when fused with the hydroxide, hydrogen is evolved and a vanadate formed. Metallic vanadium precipitates platinum, gold, and silver, from solutions of their salts, and reduces mercuric, cupric, and ferric salts to the corresponding lower salts (Marino).

When heated in an atmosphere of pure nitrogen, metallic vanadium at once absorbs this gas and is converted into the mononitride (Roscoe).

Alloys of vanadium can be prepared in the electric furnace by reducing vanadic anhydride in the presence of the second

[1] Ruff and Martin, *Zeit. angew. Chem.*, 1912, **25**, 49.
[2] Matignon and Monnet, *Compt. rend.*, 1902, **134**, 542.
[3] Marino, *Zeit. anorg. Chem.*, 1904, **39**, 152.

metal or one of its oxides.[1] It also forms an alloy with platinum. Ferrovanadium is manufactured on a commercial scale in the electric furnace in France and also in Colorado. It is used in the production of vanadium steel (see Steel).

COMPOUNDS OF VANADIUM.

Vanadium and Oxygen.

417 Vanadium forms five compounds with oxygen, analogous to the oxides of nitrogen, namely:

Vanadium suboxide	V_2O.
Vanadium monoxide, hypovanadious oxide .	VO or V_2O_2.
Vanadium sesquioxide, vanadium trioxide .	V_2O_3.
Vanadium dioxide, hypovanadic oxide . . .	VO_2 or V_2O_4.
Vanadic anhydride, vanadium pentoxide . .	V_2O_5.

All these oxides form salts, the three first acting only as basic oxides, the two highest both as acid-forming oxides and as weak basic oxides.

Some confusion exists as to the nomenclature of the various oxides of vanadium and the series of compounds derived from them. Roscoe, to mark the analogy with arsenic and phosphorus, termed the sesquioxide, V_2O_3, vanadious oxide, and its salts the vanadious salts, and to the lower oxide, VO or V_2O_2, he gave the name hypovanadious oxide. The fact that V_2O_3 acts entirely as a basic oxide and the close analogy existing between the derivatives of V_2O_3 and of VO, and the corresponding chromium compounds, has led more recent investigators[2] to term the compounds derived from V_2O_3 the vanadic salts, and those derived from VO the vanadious salts, corresponding with the chromic and chromous salts respectively. The salts formed by the oxide VO_2 with bases, termed by Roscoe hypovanadates, are now usually called vanadites, and the salts with acids containing the divalent radical VO (or the tetravalent radical V_2O_2) are known as vanadyl (or divanadyl) compounds. The more modern nomenclature has been adopted here.

418 *Vanadic Anhydride*, V_2O_5.—The preparation of this oxide from mottramite has already been described. In the pure state

[1] Moissan, *Compt. rend.*, 1896, **122**, 1297.

[2] Piccini and Marino, *Zeit. anorg. Chem.*, 1902, **32**, 57.

it is best prepared by decomposing the oxytrichloride, $VOCl_3$, with water and fusing the residue, but it can also be obtained pure by heating pure ammonium metavanadate and avoiding any reduction.[1] Vanadic anhydride crystallises in splendid yellowish-red rhombic prisms (Nordenskiöld), which have a specific gravity of 3·35 (J. J. Watts), and dissolve in about 1,000 times their weight of water, giving a yellowish solution, which does not possess any taste but turns blue litmus paper red. Vanadic anhydride fuses without decomposition in absence of organic reducing matter to a red liquid, which on cooling yields brilliant transparent reddish-yellow needles, and at the moment of crystallisation exhibits the phenomenon of incandescence.

Vanadic anhydride exists in several different modifications, which differ in solubility and other properties. When it is prepared by igniting ammonium vanadate, evaporating with nitric acid and gently heating the residue, it forms a yellow hygroscopic powder, which unites with water to form hydrates containing 1, 2, and 8 molecules of water, and dissolves in cold water to the extent of 8 grams per litre. When the oxide is heated for a long time at 440° or fused, it is converted into two different sparingly soluble modifications.[2]

Vanadic anhydride acts as a weak basic oxide as well as an acid-forming oxide. Thus it dissolves in strong acids, forming red or yellow solutions yielding crystalline compounds, which separate out on spontaneous evaporation or cooling.

Vanadic anhydride is reduced by sulphurous acid in presence of sulphuric acid, and by evaporation with hydrochloric acid, to VO_2; magnesium and hydrochloric acid, or evaporation with hydriodic acid, reduce it to V_2O_3, whilst zinc and hydrochloric acid carry the reduction a stage further, to VO.

Vanadic anhydride has been used in the preparation of aniline black, and its use has been suggested in the electrolytic oxidation and reduction of various organic compounds in an acid bath, *e.g.*, the manufacture of quinone from aniline, &c.[3] It also greatly accelerates certain oxidation processes, such as the action of nitric acid on sugar, the oxidation of alcohol by atmospheric oxygen, &c.[4]

[1] Matignon, *Chem. Zeit.*, 1905, **29**, 986.

[2] Ditte, *Compt. rend.*, 1885, **101**, 698.

[3] German Patent, 172654 (15/9/03).

[4] Moeser and Lindenbaum, *J. pr. Chem.*, 1907, [2], **75**, 146 ; German Patent, 183022 (18/8/05).

The Vanadic Acids and their Salts.

419 *Normal Vanadic Acid*, H_3VO_4, is not known.

Metavanadic Acid, HVO_3, was discovered by Gerland.[1] It forms a fine yellow pigment, sometimes termed vanadium bronze, and is employed in place of gold bronze. It is obtained in the form of brilliant scales of a golden or orange colour by boiling aqueous sulphurous acid with copper vanadate, prepared by the double decomposition of ammonium metavanadate and copper sulphate. A mixture of brown and orange-yellow crystals is obtained, and on continuing the ebullition with more sulphurous acid, the brown crystals dissolve, the yellow metavanadic acid being insoluble.

Vanadium bronze may also be prepared by adding a solution of ammonium vanadate to one of copper sulphate containing excess of ammonium chloride until a permanent precipitate is formed, and then gently heating to 75°, when the yellow scales are slowly deposited, and after the lapse of a few hours nearly the whole of the vanadium is precipitated. The larger the quantity of material employed and the slower the action takes place, the finer is the colour of the bronze.[2]

If the freshly prepared solution of copper vanadate be quickly evaporated in a flat dish, a crystalline residue is obtained which is soluble in water, and when this solution is dialysed for some days a clear solution of pure vanadic acid is obtained which remains clear when heated, and deposits the red amorphous pentoxide on evaporation.

Pyrovanadic Acid, $H_4V_2O_7$, is a brown precipitate closely resembling ferric hydroxide, obtained by treating a solution of an acid vanadate with nitric acid. When air-dried it possesses the above composition. It is, however, unstable and loses half its water when dried over sulphuric acid (v. Hauer).

Hexavanadic Acid, $H_4V_6O_{17} = 6V_2O_5,2H_2O$.—When a solution of pervanadic acid is allowed to stand it loses oxygen and forms an acid yellow liquid, which probably contains hexavanadic acid. The solution is unstable and soon deposits a brown precipitate of vanadium pentoxide.[3]

The Vanadates.—Inasmuch as Berzelius thought that the oxide VO was the metal, and, therefore, considered the highest

[1] *Proc. Manch. Phil. Soc.*, 1873, **12**, 50.
[2] *Ber.*, 1876, **9**, 874.
[3] Düllberg, *Zeit. physikal. Chem.*, 1903, **45**, 170.

oxide to be a trioxide, he likewise assumed that the vanadates corresponded to the chromates. In addition to the so-called normal salts examined by him, two other series were described by v. Hauer,[1] which, appearing to correspond to the dichromates and trichromates, received names analogous to these. After the true formula of the highest oxide of vanadium had been ascertained to be V_2O_5, it was evident that the so-called normal vanadates corresponded to the metaphosphates, and it was found possible to prepare both the ortho- and pyro-vanadates analogous to the corresponding phosphates. v. Hauer's salts would then most naturally be formulated as tetra- and hexa-vanadates, $Na_2V_4O_{11}$ and $Na_2V_6O_{16}$, but it is probable from the researches of Düllberg on the molecular weights and conductivities of these salts, that they are in reality acid salts derived from hexavanadic acid, $H_4V_6O_{17}$, the normal salt of which, $Na_4V_6O_{17}$, is also known. It is probable that the potassium and ammonium tetravanadates are also in reality hexavanadates, but these have not yet been investigated. Thus we have :

(1) Sodium Metavanadate	$NaVO_3$.
(2) Sodium Orthovanadate	Na_3VO_4.
(3) Sodium Pyrovanadate	$Na_4V_2O_7$.
(4) Sodium Tetravanadate (v. Hauer) .	$Na_3HV_6O_{17}$.
(5) Sodium Hexavanadate „	$Na_2H_2V_6O_{17}$.

Other polyvanadates of more complicated composition have also been described.[2]

Although the first three classes of vanadates correspond in composition to the phosphates, the order of stability of the soluble vanadates in aqueous solution differs remarkably from that of the phosphates, the metavanadates being the most stable and the orthovanadates the least stable, whereas in the phosphorus series the order of stability is the reverse of this. At a high temperature, on the other hand, the orthovanadate is the most stable, being formed when vanadium pentoxide is fused with an alkali carbonate, the meta-salt being produced when a solution of an alkali carbonate is boiled with vanadium pentoxide.

The property which serves best to distinguish the ortho- from the meta-vanadates is the colour of the respective copper salts.

[1] *J. pr. Chem.*, 1856, **69**, 385 ; 1859, **76**, 156, 929 ; 1860, 80, 324.
[2] Carnelley, *Journ. Chem. Soc.*, 1873, **26**, 323.

Copper orthovanadate possesses a blue-green colour, whilst the metavanadate is a light-yellow crystalline powder.

The alkali pyrovanadates are soluble, and can be readily obtained by fusing one molecule of vanadium pentoxide with two molecules of the carbonate of an alkali metal, dissolving, and crystallising. They are likewise obtained by the decomposition of an aqueous solution of the corresponding orthovanadate. The pyrovanadates of the heavy metals are usually insoluble in water, and possess properties generally similar to those of the corresponding orthovanadates.

The metavanadates are usually yellow: some of them, especially those of the alkaline earths, zinc, cadmium, and lead, are converted into colourless isomeric modifications, in the solid state under water, in aqueous solution, and especially in the presence of alkali carbonates. The metavanadates of the alkali metals are colourless, and on treatment with an acid give rise to anhydro-salts, which have a fine yellowish-red colour. The metavanadates of ammonium, potassium, sodium, barium, and lead are but sparingly soluble in water. The other metavanadates are more soluble. It is probable that sodium metavanadate has the molecular formula $Na_3V_3O_9$, thus corresponding with the trimetaphosphate (Düllberg). The following are the properties of the most important members of these three classes of vanadates.

Potassium Metavanadate, KVO_3, dissolves slowly in cold and readily in hot water, and with difficulty in caustic potash. When it is boiled with water and vanadium pentoxide, or fused with the latter, *potassium tetravanadate*, $K_2V_4O_{11},3H_2O$, or $K_3HV_6O_{17},4H_2O$ (Düllberg), is obtained, crystallising in broad reddish-yellow tablets. This salt is slightly soluble in cold and very easily soluble in hot water.

Sodium Orthovanadate, Na_3VO_4.—This salt crystallises with 16, 12, 10, and $8H_2O$, and in the form with $12H_2O$ is isomorphous with sodium orthophosphate. It has a strongly alkaline reaction, and in aqueous solution is completely hydrolysed to caustic soda and sodium pyrovanadate:

$$2Na_3VO_4 + H_2O = Na_4V_2O_7 + 2NaOH.$$

Sodium Pyrovanadate, $Na_4V_2O_7,18H_2O$, crystallises in large six-sided tablets, is easily soluble in water, and is precipitated by alcohol from its aqueous solution in pearly scales. It fuses

more easily than the orthovanadate, and is first formed in the preparation of the latter salt.

Sodium Metavanadate, $NaVO_3$, resembles the potassium salt, and is converted in a similar manner into *sodium tetravanadate*, $Na_2V_4O_{11},9H_2O$, or $Na_3HV_6O_{17},13H_2O$ (Düllberg), which separates out in beautiful large orange-red crystals. This salt is only slightly soluble in water, but possesses such powerful colouring properties that 1 part of it is sufficient to impart a yellow tint to 200,000 parts of water. It effloresces on exposure to the air, becoming of a reddish-brown tint, and melts at a dark red heat, solidifying to a dark red amorphous mass.

Ammonium Metavanadate, NH_4VO_3, is the most important vanadate. It is obtained by dissolving the pentoxide in an excess of ammonia and evaporating, or by precipitating with alcohol, in which it is insoluble. It forms colourless transparent crystalline crusts, and is insoluble in concentrated solution of ammonium chloride, and accordingly is precipitated when a lump of ammonium chloride is allowed to remain in a solution of a metavanadate or pyrovanadate:

$$Na_4V_2O_7+4NH_4Cl=2NH_4VO_3+2NH_3+H_2O+4NaCl.$$

The solution of this salt becomes of a deep black tint when treated with tincture of galls, and Berzelius originally suggested the use of this liquid as an ink. This ink is, however, not permanent, "for letters thus written by Berzelius are now quite illegible" (Wöhler). It has also been used in dyeing with aniline black, since its presence greatly facilitates the oxidation of the aniline hydrochloride on which the formation of the colouring matter depends. It is, however, no longer used for this purpose.

Ammonium Tetravanadate, $(NH_4)_2V_4O_{11},4H_2O$, or $(NH_4)_3HV_6O_{17},5\frac{1}{2}H_2O$, is obtained by the addition of acetic acid to a boiling solution of the metavanadate until the precipitate redissolves. The salt separates out from the yellowish-red liquid on cooling in large transparent orange-red crystals. If it be recrystallised from water containing acetic acid, splendid red crystals of *ammonium hexavanadate*, $(NH_4)_2V_6O_{16},6H_2O$, or $(NH_4)_2H_2V_6O_{17},5H_2O$, are obtained.

Calcium Pyrovanadate, $2Ca_2V_2O_7,5H_2O$, is a white amorphous precipitate obtained by double decomposition of the corresponding sodium salt with calcium chloride. If the solution of sodium orthovanadate be precipitated by calcium

chloride, the same salt is obtained mixed with calcium hydroxide, the orthovanadate being at once decomposed according to the equation:

$$Ca_3(VO_4)_2 + H_2O = Ca_2V_2O_7 + Ca(OH)_2.$$

Lead Orthovanadate, $Pb_3(VO_4)_2$, is a nearly white insoluble precipitate obtained by adding a solution of lead acetate to one of sodium orthovanadate. This salt occurs in nature combined with lead chloride as vanadinite, $3Pb_3(VO_4)_2,PbCl_2$ or $Pb_3(VO_4)_2,Pb_2(VO_4)Cl$. This mineral crystallises in hexagonal prisms, having a reddish-brown colour, and is isomorphous with apatite. It has a specific gravity of from 6·6 to 7·2, and frequently contains some phosphoric acid. It was found by Del Rio in Zimapan in Mexico, and occurs also at Leadhills in Scotland, in Carinthia, and in the Urals. It may be obtained artificially by fusing together lead oxide, vanadium pentoxide, and lead chloride, in the right proportions. The fused mass contains druses, in which thin needle-shaped crystals are contained. If boiled with water it falls to a crystalline powder consisting of microscopic hexagonal prisms, possessing the waxy lustre and the yellowish colour of natural vanadinite, and having a specific gravity of 6·7 (Roscoe).

Lead Pyrovanadate, $Pb_2V_2O_7$, is found in South America as descloizite in rhombic crystals, which have an orange-green or black colour, a bronze lustre, and a specific gravity of 5·839. It usually contains zinc, iron, manganese, and copper as impurities. If a solution of sodium pyrovanadate be precipitated with lead acetate, the basic salt $Pb_5V_4O_{15}$ is thrown down as a light-yellow precipitate.

Lead Metavanadate, $Pb(VO_3)_2$, is obtained as a yellow precipitate when a solution of a metavanadate is mixed with one of lead acetate. The mineral dechenite consists chiefly of this compound, a portion of the lead, however, being usually replaced by zinc. It occurs together with lead ores, forming yellow, brown, or deep-red reniform masses, having a specific gravity of 5·6 to 5·8.

Lead Tetravanadate, $Pb_2V_4O_{11}$, is obtained by precipitating the corresponding potassium salt with lead nitrate in the form of a reddish-yellow precipitate slightly soluble in water.

Copper Orthovanadate, $Cu_3(VO_4)_2,H_2O$, occurs as the mineral volborthite, in which a part of the copper is replaced by calcium; it crystallises in small yellow or green hexagonal tablets, having a

specific gravity of 3·55, and is found in Thuringia and in the Urals. *Copper Pyrovanadate,* $Cu_2V_2O_7$, is a yellow crystalline precipitate, whilst *copper metavanadate* is an apple-green precipitate.

Silver Orthovanadate, Ag_3VO_4, is obtained by precipitating a freshly prepared solution of the sodium salt with silver nitrate. It is a deep orange-red coloured precipitate, which is easily soluble in nitric acid and in ammonia.

Silver Pyrovanadate, $Ag_4V_2O_7$, is a heavy yellow powder.

Silver Metavanadate, $AgVO_3$, forms a pale yellow gelatinous precipitate.

Vanadic acid, like phosphoric acid, yields complex compounds with stannates,[1] tungstates, and molybdates, as well as with phosphates and arsenates.[2]

Pervanadic Acid and the Pervanadates.—The alkali metavanadates are readily converted by hydrogen peroxide into per-salts of the formula $R'VO_4$, many of which have been prepared pure. They are decomposed by dilute acids with evolution of one atomic proportion of oxygen.[3]

Pervanadic Acid, HVO_4, is formed when vanadium pentoxide is added to hydrogen peroxide in dilute sulphuric acid solution. A deep-red coloured liquid is formed,[4] which deposits unstable yellow crystals of the per-acid.[5]

Potassium Pervanadate, KVO_4, is a yellow microcrystalline precipitate, obtained by dissolving potassium metavanadate in a solution of hydrogen peroxide containing sulphuric acid, and precipitating with alcohol.

Barium metapervanadate, $Ba(VO_4)_2$, is obtained as an amorphous yellow precipitate, when a solution of barium chloride is added to a saturated solution of ammonium metavanadate in 30 per cent. hydrogen peroxide. Other salts have been prepared in a similar manner; they are characterised by being bright yellow or deep orange.

More complex compounds are formed by the action of alkalis and hydrogen peroxide on the pervanadates, and these are probably salts of a pyropervanadic acid with the peroxides of

[1] Prandtl, *Ber.*, 1907, **40**, 2125.

[2] For an account of these complex derivatives see the monograph by Ephraim quoted on p. 912.

[3] Scheuer, *Zeit. anorg. Chem.*, 1898, **16**, 284; Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 210, 472.

[4] Werther, *J. pr. Chem.*, 1861, **83**, 195.

[5] Pissarjewsky, *Zeit. physikal. Chem.*, 1903, **43**, 173.

the alkali metals. The ammonium salt, $(NH_4)_4V_2O_{11}$, and the potassium salt, $K_8V_5O_{26},2H_2O$, have been prepared in this way.[1] Complex oxygenated products have also been obtained by the action of hydrogen peroxide on the compound of vanadyl trifluoride with potassium fluoride,[2] $VOF_3,2KF$.

The Lower Oxides of Vanadium.

420 *Vanadium Suboxide*, V_2O, is formed by the prolonged exposure of finely divided metallic vanadium to the air. It is a brown substance, which, when heated in the air, is gradually converted into the higher oxides. No salts of this oxide have been prepared.

Vanadium Monoxide or *Hypovanadious Oxide*, VO or V_2O_2.—In its power of uniting with oxygen vanadium surpasses even uranium,[3] and, like uranium, it can be separated from its last portions of oxygen only with extreme difficulty. The oxide VO is, moreover, found to enter as a radical into many compounds, so that the name vanadyl (VO) may appropriately be given to it. This substance, which was regarded by Berzelius as metallic vanadium, may be prepared by reducing the higher oxides with potassium, or by passing the vapour of vanadyl trichloride, $VOCl_3$, mixed with excess of hydrogen, through a combustion tube containing red-hot carbon.[4] Thus obtained it forms a light-grey glistening powder or a lustrous metal-like crust, having a specific gravity of 3·64. It is brittle, difficultly fusible, and conducts electricity. Heated to redness, it takes fire in the air and burns to the sesquioxide V_2O_3, whilst when heated in chlorine the oxytrichloride $VOCl_3$ is formed. It is insoluble in water, but dissolves in acids, yielding the corresponding salts. These may also be obtained in solution by the action of nascent hydrogen, evolved by metallic zinc, cadmium, or sodium amalgam, upon a solution made by dissolving vanadium pentoxide in hot concentrated sulphuric acid and then diluting with water, or by the electrolytic reduction of a similar solution. The liquid rapidly changes colour, passing through all shades of blue and

[1] Melikoff and Pissarjewsky, *Zeit. anorg. Chem.*, 1899, **19**, 405: Pissarjewsky, *ibid.*, 1903, **32**, 341.

[2] Melikoff and Kasanezky, *Zeit. anorg. Chem.*, 1901, **28**, 242.

[3] Péligot, *Ann. Chim. Phys.*, 1842, [3], **5**, 5; 1844 [3], **12**, 549.

[4] Schafarik, *Annalen*, 1859, **109**, 85.

green until after some time it assumes a permanent lavender or violet tint. In order to prove that this solution really contains the vanadium as a divalent element, a standard solution of potassium permanganate is added until a permanent pink colour is obtained and the vanadium has reached the highest degree of oxidation, when it is found that for every two atoms of metal three atoms of oxygen have been added. This solution of the sulphate absorbs oxygen with such avidity as to bleach indigo and other vegetable colouring matters as quickly as chlorine. The solution in hydrochloric acid has been suggested as a reagent for removing arsenic from hydrochloric acid, the whole of the arsenic being precipitated in the free state when the impure hydrogen chloride is passed through the solution.[1] On allowing the neutralised lavender-coloured solution to stand exposed to the air for a few seconds, the colour changes to a deep chocolate-brown: and so rapid is the alteration of colour, when but little free acid is present, that such a lavender solution may serve as a reagent for the detection of free oxygen not inferior in delicacy to an alkaline pyrogallate. The changes in colour which the yellow sulphuric acid solution of vanadium pentoxide undergoes on reduction are exceedingly characteristic, and may be divided into eight stages as follows:

Stage.	Colour.	Reaction.	State of Oxidation of the Metal.
I.	Yellow	Acid	V_2O_5.
II.	Green	Acid	V_2O_5—VO_2.
III.	Bluish-green	Acid	V_2O_5—VO_2.
IV.	Blue	Acid	VO_2.
V.	Greenish-blue	Acid	VO_2—V_2O_3.
VI.	Green	Bleaches slightly	V_2O_3—VO.
VII.	Bluish-violet	Bleaches strongly	V_2O_3—VO.
VIII.	Lavender or violet	Bleaches strongly	VO.

[1] German Patent, 164355 (15/4/04).

Thus the salts derived from the pentoxide are yellow; the divanadyl salts blue; the sesqui-salts are green; and the vanadious salts lavender-coloured.

Vanadium Sesquioxide or *Vanadium Trioxide*, V_2O_3, is obtained by heating the pentoxide in hydrogen, or by igniting the same oxide in a carbon crucible. It is also formed when vanadyl trichloride and hydrogen are passed through a red-hot tube, and when the pentoxide is heated in the oxyhydrogen flame.[1] It is a black powder, which may by pressure be united to form a coherent mass which conducts electricity. It undergoes oxidation when exposed to the air, not only being pyrophoric when warm, but also slowly taking up oxygen when exposed in the air at ordinary temperatures, and being converted into small dark indigo-coloured crystals of the dioxide VO_2. It has a specific gravity of 4·7. When ignited in chlorine gas it is converted into vanadium oxytrichloride, $VOCl_3$, and vanadium pentoxide:

$$3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3.$$

It is insoluble in most acids, but the corresponding sulphate may be obtained in solution by the reducing action of nascent hydrogen, evolved from metallic magnesium, on a solution of vanadium pentoxide in sulphuric acid. A green liquid is thus obtained, the further reduction observed with zinc, cadmium, and sodium amalgam not taking place with magnesium. The green solution may likewise be obtained by the partial oxidation of the lavender-coloured solution of vanadious sulphate, VSO_4. If a current of air be passed through such a solution, in which the free acid has been neutralised by an excess of zinc and the remaining metallic zinc removed, the liquid attains a permanent brown colour, which on the addition of a few drops of acid turns green; the solution then contains the sesquisulphate.

Vanadium Dioxide or *Hypovanadic Oxide*, VO_2 or V_2O_4.—This oxide can be prepared either by the oxidation of the monoxide, VO, in the air, or by the partial reduction of the pentoxide. It is readily converted by potassium permanganate into the pentoxide, and advantage is taken of this fact in the volumetric estimation of vanadium. It is a lustrous steel-coloured powder and dissolves in acids, forming solutions of the vanadyl salts, which possess a bright blue colour. Solutions of these salts are also

[1] Read, *Journ. Chem. Soc.*, 1894, **65**, 314.

produced by the action of moderate reducing agents, such as sulphur dioxide and sulphuretted hydrogen or oxalic acid upon solutions of vanadic acid in sulphuric acid. They may also be obtained by passing a current of air through acid solutions of the vanadious salts until a permanent blue colour is attained. The oxide may likewise be prepared by the electrolysis of the fused pentoxide, or by the ignition of the oxychloride, $V_2O_2Cl_4,5H_2O$, in a current of carbon dioxide:

$$V_2O_2Cl_4 + 5H_2O = 2VO_2 + 4HCl + 3H_2O.$$

Divanadyl Hydroxide or *Hypovanadic Hydrate*, $V_2O_4,7H_2O$ or $V_2O_2(OH)_4,5H_2O$, forms a greyish-white precipitate, obtained when a solution of vanadyl sulphate or chloride is cautiously precipitated with a cold solution of sodium carbonate. When dried it is a black amorphous mass, having a glassy fracture. This on heating to 100° loses four molecules of water, leaving the hydrate, $V_2O_4,3H_2O$. A hydrate containing $2H_2O$ is obtained as a pink crystalline powder by boiling a solution of the dioxide, VO_2, in sulphurous acid.[1] Vanadium dioxide acts both as a basic, and as an acid-forming oxide. When dissolved in acids the vanadyl salts are formed,[2] whilst with alkalis the vanadites or hypovanadates are produced.

The *vanadites* or *hypovanadates* are all insoluble except those of the alkali metals, which are not derived from the normal hypovanadic acid, $H_4V_2O_6$, but from the partial anhydrides, $H_2V_2O_5$ and $H_2V_4O_9$. The alkali vanadites are obtained by adding an excess of caustic alkali to a concentrated solution of vanadyl sulphate or chloride.[3] The dark-brown solution thus obtained with potash deposits *potassium vanadite*, $K_2V_4O_9,7H_2O$, in reddish-brown crystalline scales which, after washing first with potash solution, and then with alcohol, may be dried between filter-paper. This salt is permanent in the air, and very soluble in water, yielding a dark-brown solution.

Sodium Vanadite, $Na_2V_4O_9,7H_2O$, is prepared in a similar way to the potassium salt, and exhibits analogous properties.

Ammonium Vanadite, $(NH_4)_2V_4O_9,3H_2O$, is obtained as a dark-brown crystalline precipitate by adding a vanadyl sulphate solution to ammonia; it dissolves in water, yielding an almost black solution (Crow).

[1] Gain, *Compt. rend.*, 1906, **143**, 823.

[2] Guyard, *Bull. Soc. chem.*, 1876, [2], **25**, 350.

[3] See also Koppel and Goldmann, *Zeit. anorg. Chem.*, 1903, **36**, 281.

On the addition of solutions of soluble vanadites to solutions of salts of the heavy metals, insoluble precipitates are formed.

Vanadium and Fluorine.

421 The oxides, V_2O_3, VO_2, and V_2O_5, all dissolve in hydrofluoric acid, but only the trifluoride, $VF_3,3H_2O$, and the oxydifluoride, VOF_2, have been isolated. A very large number of double salts of these compounds and of the oxyfluorides VO_2F and VOF_3 with hydrofluoric acid, metallic fluorides, and vanadium pentoxide have been described.[1] Only a few of the most characteristic are mentioned here.

Vanadium Trifluoride, $VF_3,3H_2O$, crystallises from the dark-green solution of vanadium trioxide in hydrofluoric acid, in dark-green readily soluble octahedra. The *double potassium salt*, $2KF,VF_3,H_2O$, is a bright green crystalline powder, which is precipitated when a solution of potassium fluoride is added to one of vanadium trifluoride.

Vanadium Oxydifluoride, VOF_2, is formed when the tetroxide is dissolved in hydrofluoric acid, and separates in blue prismatic crystals containing water. Several double salts with the fluorides of sodium, potassium, and ammonium may be prepared by adding solutions of these fluorides to the blue solution of the oxydifluoride (Petersen).

Potassium Vanadium Dioxyfluoride, $2KF,VO_2F$, is obtained by evaporating a solution of vanadium pentoxide in hydrofluoric acid almost to dryness, and adding it to potassium fluoride. It crystallises in golden-yellow six-sided prisms.

Vanadium pentoxide also dissolves easily in a solution of hydrogen potassium fluoride with evolution of heat, and on cooling yellowish globular masses separate out, consisting of pearly, probably hexagonal crystals, which have the composition $3KF,2VO_2F,H_2O$.

Ammonium Vanadium Dioxyfluoride, $3NH_4F,VO_2F$, is formed when a solution of vanadium pentoxide in hydrofluoric acid is nearly neutralised with ammonia; it separates in large golden-yellow crystals.

Zinc Vanadium Dioxyfluoride, $ZnF_2,VO_2F,7H_2O$, is formed by dissolving zinc carbonate and vanadium pentoxide in hydrofluoric acid. The salt crystallises in hard, yellow, triclinic prisms.

[1] Petersen, *J. pr. Chem.*, 1889, [2], **40**, 193, 271. See also Piccini and Giorgis, *Journ. Chem. Soc.*, 1889, **56**, 214; and Baker, *Journ. Chem. Soc.*, 1878, **33**, 388.

Vanadium and Chlorine.

422 The only compounds of vanadium and chlorine described before 1867 were oxychlorides. Three chlorides free from oxygen have been subsequently obtained either by the action of chlorine on the nitride of vanadium, VN, or by distilling the oxychlorides over charcoal.[1] The following chlorides and oxychlorides of vanadium are now known:

Chlorides.

Vanadium tetrachloride .	VCl_4.
„ trichloride . .	VCl_3 or V_2Cl_6.
„ dichloride . .	VCl_2 or V_2Cl_4.

Oxychlorides.

Vanadium oxytrichloride .	$VOCl_3$.
„ oxydichloride .	$VOCl_2$.
„ oxymonochloride	VOCl.
Divanadyl monochloride .	V_2O_2Cl.
„ tetrachloride .	$V_2O_2Cl_4,5H_2O$.
Divanadium trioxydichloride	$V_2O_3Cl_2,4H_2O$.

Vanadium Tetrachloride, VCl_4, is formed when metallic vanadium or the mononitride is heated to redness in an excess of chlorine. It is best prepared by repeatedly passing the vapour of vanadium oxytrichloride, together with an excess of dry chlorine, over a long column of pure sugar charcoal heated to dull redness. It can also be prepared by treating the crude vanadium, prepared as already described by the aid of aluminium, with chlorine and removing the oxytrichloride, which is also formed, by fractional distillation.[2] Vanadium tetrachloride is a dark, brownish-red, thickish liquid, which evolves white fumes when exposed to moist air. It boils at 154° with partial decomposition, losing chlorine and leaving a residue of the trichloride. This decomposition takes place also at the ordinary temperature, especially on exposure to light. It does not solidify at −18°; its specific gravity at 0° is 1·8584, and its vapour density

[1] Roscoe, *Phil. Trans.*, 1869, **159**, 679.

[2] Koppel, Goldmann and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 345.

at 205° is 6·69, the calculated vapour density being 6·675. When thrown into water the tetrachloride is at once decomposed, yielding a blue solution of vanadyl chloride.

The tetrachloride heated in excess of chlorine splits up into trichloride and free chlorine, so that vanadium does not appear to form a penta-compound with chlorine.

Vanadium Trichloride, VCl_3.—The foregoing compound easily decomposes, as has been stated, into this body and chlorine. The trichloride is obtained either by the slow decomposition of the tetrachloride at the ordinary temperature or at its boiling point, or, together with the dichloride when the vapour of the tetrachloride mixed with hydrogen is passed through a red-hot tube, as well as when the trisulphide is heated in chlorine.[1] It is a solid substance, crystallising in fine peach-blossom coloured, shining tablets, closely resembling in appearance the crystals of chromium trichloride. It is non-volatile when heated in hydrogen, and decomposes when heated in the air, the pentoxide being formed. Ignited in a current of hydrogen it first loses one atom of chlorine, forming the dichloride, VCl_2, parting at a higher temperature with the whole of its chlorine, and leaving a residue of metallic vanadium as a lustrous grey powder. It is extremely hygroscopic, instantly deliquescing on exposure to moist air to a dark-brown liquid, which on addition of a drop of hydrochloric acid becomes green. The specific gravity of vanadium trichloride is 3·0; it readily dissolves in absolute alcohol and in ether, forming green-coloured solutions.

A hydrated compound of the composition $VCl_3,6H_2O$ can be obtained as a green crystalline powder by evaporating in vacuo a solution of vanadium sesquioxide in hydrochloric acid,[2] or by dissolving vanadium pentoxide in hydrochloric acid, reducing the solution electrolytically with a platinum cathode and saturating the green solution with hydrochloric acid.[3] The salt decomposes when heated before all the water has been driven off. The aqueous solution rapidly oxidises in the air. Sparingly soluble double salts are formed with the chlorides of the alkali metals,[4] the potassium salt having the formula $VCl_3,2KCl,H_2O$.

Vanadium Dichloride or *Vanadious Chloride*, VCl_2.—This is a

[1] Halberstadt, *Ber.*, 1882, **15**, 1619.
[2] Locke and Edwards, *Amer. Chem. J.*, 1898, **20**, 594.
[3] Piccini and Brizzi, *Zeit. anorg. Chem.*, 1899, **19**, 394.
[4] Stähler *Ber.*, 1904, **37**, 4411.

solid body, crystallising in fine apple-green coloured plates, having a micaceous lustre and a hexagonal form. It is prepared by passing vanadium tetrachloride, mixed with dry and pure hydrogen, through a glass tube heated to dull redness, and is also formed together with silicon tetrachloride when vanadium silicide, VSi_2, is heated in chlorine.[1] Its specific gravity at 18° is 3·23. It is very deliquescent, yielding a lavender-coloured solution of vanadium dichloride, which possesses bleaching properties (p. 927). A violet solution containing the chloride can be obtained by the electrolytic reduction of the trichloride. When it is evaporated or when hydrochloric acid is added, hydrogen is evolved and the trichloride is formed, the reaction being extremely vigorous when a piece of platinum foil is placed in the acid liquid. Vanadious chloride is therefore a more vigorous reducing agent than chromous chloride.[2] When the dichloride is heated to whiteness in a current of dry ammonia, vanadium mononitride is obtained in bronze-coloured pseudomorphous crystals.

Vanadium Oxytrichloride or *Vanadyl Trichloride*, $VOCl_3$, —This compound, corresponding to phosphorus oxychloride, is obtained either by the action of chlorine on the oxides VO and V_2O_3 as already described, or by heating a mixture of the pentoxide and charcoal in a current of chlorine:

$$V_2O_5+3C+3Cl_2=2VOCl_3+3CO.$$

In the latter case the resulting liquid is red-coloured from the presence of tetrachloride, and is best purified by rectification over clean sodium in a current of carbon dioxide. It is also formed[3] when dry hydrogen chloride is passed over a mixture of vanadic and phosphoric anhydrides at 60—80°, and a solution in acetic acid may be obtained by treating vanadium pentoxide with a solution of hydrogen chloride in glacial acetic acid.[4] Vanadyl trichloride is a bright lemon-yellow coloured mobile liquid, boiling at 126·7° and having a specific gravity at 14° of 1·841. It does not solidify at −15°. The specific gravity of its vapour is 6·108 at 186°, the calculated specific gravity being 6·003.

On exposure to moist air vanadyl trichloride emits vapours of a cinnabar-red colour, and is soon decomposed in the presence

[1] Moissan and Holt, *Compt. rend.*, 1902, **135**, 78.
[2] Piccini and Marino, *Zeit. anorg. Chem.*, 1902, **32**, 68.
[3] Ephraim, *Zeit. anorg. Chem.*, 1903, **35**, 66.
[4] Koppel and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 352.

of moisture into vanadic and hydrochloric acids. When a small quantity of water is added it becomes thick and blood-red coloured owing to the formation of vanadic acid. A large quantity of water, however, yields a clear yellow solution.[1] When the oxychloride is ignited in a current of dry ammonia gas, vanadium mononitride is obtained. Vanadium oxychloride combines with ether at 70°, forming a compound crystallising in long red needles and having the composition $VCl_3(OC_2H_5)_2$.[2]

When vanadium oxychloride is heated with zinc to 400°, vanadium dioxide and *vanadyl dichloride*, $VOCl_2$, are formed; the latter crystallises in green tablets which deliquesce on exposure to moist air. The same compound is formed when the vapour of vanadyl trichloride and hydrogen are passed through a red-hot tube. In this case *vanadyl monochloride*, VOCl, and *divanadyl monochloride*, V_2O_2Cl, are likewise formed, the former as a flocculent brown powder insoluble in water, and the latter in the form of a yellow crystalline powder resembling mosaic gold. The molecular formulæ of these bodies are not known. Vanadyl dichloride forms double compounds with two or four molecules of the hydrochlorides of pyridine and quinoline.[3]

Divanadyl Tetrachloride, $V_2O_2Cl_4,5H_2O$,$(VOCl_2,2{\cdot}5H_2O)$.—When vanadium pentoxide is dissolved in hot concentrated hydrochloric acid, chlorine is evolved and a green solution is obtained which becomes blue with deposition of sulphur when sulphuretted hydrogen is passed through the liquid. A brown amorphous deliquescent mass is obtained on evaporation, possessing the above composition. It dissolves in water yielding a blue solution; but when treated with strong hydrochloric acid or alcohol the solution is brown, and this change may possibly be due to the existence of two different hydrates.[4]

A compound of the formula $V_2O_3Cl_2,4H_2O$ has also been obtained as a dark green deliquescent mass, by the action of hydrochloric acid on vanadium pentoxide.[5]

Vanadium and Bromine and Iodine.

423 *Vanadium Tribromide*, VBr_3.—This is the only known compound of the above elements. It condenses as a greyish-

[1] See Agafonoff, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 649.
[2] Bedson, *Journ. Chem. Soc.*, 1876, i, 309.
[3] Koppel, Goldmann and Kaufmann, *Zeit. anorg. Chem.*, 1905, **45**, 345.
[4] Crow, *Journ. Chem. Soc.*, 1876, ii., 453.
[5] Ditte, *Compt. rend.*, 1886, **102**, 1310.

black compact amorphous sublimate, when dry bromine vapour is passed in excess over vanadium nitride or over a mixture of vanadium trioxide and charcoal heated to redness. It is a very unstable compound, losing bromine even at the ordinary temperature in dry air, and deliquescing rapidly on exposure to moist air.

The hydrated bromide, $VBr_3,6H_2O$, and the corresponding iodide can be prepared in a similar manner to the hydrated chloride, which they closely resemble.

Vanadyl Tribromide, $VOBr_3$, obtained by passing dry bromine vapour over vanadium sesquioxide heated to redness, is a dark-red transparent liquid, having a density of 2·967 at 0°. It may be distilled under diminished pressure, passing over without decomposition at a temperature of about 130° under a pressure of 100 mm. When heated under the ordinary atmospheric pressure it suddenly solidifies at 180°, decomposing into free bromine and *vanadyl dibromide*, $VOBr_2$, which is a brownish-yellow powder.

Divanadyl Tetra-iodide, $V_2O_2I_4,8H_2O$, is formed by the action of hydriodic acid on vanadium pentoxide as a dark deliquescent mass.[1]

Vanadium pentoxide also appears to form a double compound with iodine pentoxide.

Vanadium and Sulphur.

424 The sulphides of vanadium correspond to the oxides.[2]

Berzelius described a persulphide and a bisulphide of vanadium. Both of these, when prepared by precipitation according to the methods given by him, seem to be mixtures of various oxysulphides. His bisulphide prepared in the dry way is in reality the trisulphide V_2S_3.

Vanadium Monosulphide, VS, is formed when the sesquisulphide is strongly heated in a current of hydrogen. It forms a brownish-black powder or glistening brown scales, which dissolve slowly in dilute, but quickly in strong nitric acid. It dissolves gradually in alkali hydrosulphides yielding a violet solution.

Vanadium Sesquisulphide or *Trisulphide*, V_2S_3.—This was the only vanadium salt free from oxygen prepared by Berzelius. He obtained it by heating the sesquioxide in a current of sulphuretted

[1] Ditte, *Compt. rend.*, 1886, **102**, 1310.
[2] Kay, *Journ. Chem. Soc.*, 1880, **37**, 728.

hydrogen. It can in like manner be prepared from the pentoxide, the oxychloride, or any of the chlorides, but it is best obtained by acting on the ignited pentoxide with carbon disulphide vapour. It is a greenish-black powder possessing properties similar to those of the monosulphide, VS.

Vanadium Pentasulphide, V_2S_5, is formed by heating the foregoing with sulphur to 400°. It is a black powder which on heating in a current of carbon dioxide yields sulphur and the sesquioxide (Kay).

Ammonium Thiovanadate, $(NH_4)_3VS_4$, is obtained by passing sulphuretted hydrogen into a cooled solution of ammonium metavanadate in ammonia of specific gravity 0·898. The crystals resemble those of potassium permanganate. If weaker ammonia be employed, *ammonium hexasulphopyrovanadate*, $(NH_4)_4V_2S_6O$, is formed in dark-green crystals.

Several sodium and potassium salts of a similar character have been prepared from the corresponding meta- and pyrovanadates.[1]

Vanadyl or *Hypovanadic Sulphite*, $6VO_2,4SO_2,9H_2O$, is prepared by reducing barium vanadate with sulphur dioxide, and filtering from the barium sulphate, formed according to the equation:

$$Ba(VO_3)_2 + H_2SO_3 = BaSO_4 + H_2O + 2VO_2.$$

When the filtrate is evaporated in an atmosphere of sulphur dioxide, the sulphite separates as a dark blue crystalline powder, which decomposes when preserved. It forms two series of double salts with the alkali sulphites.[2]

Vanadious Sulphate, $VSO_4,7H_2O$, can be prepared by the electrolytic reduction of the blue solution obtained by the action of sulphur dioxide on vanadic anhydride in the presence of sulphuric acid. In order to obtain this salt in the pure state the greatest precautions must be taken to exclude oxygen. The blue solution gradually becomes green, then blue again, and finally violet as the reduction proceeds. It is then evaporated in vacuo, and the crystals separated and dried with filter paper in an atmosphere of carbon dioxide. The salt is thus obtained in reddish-violet monoclinic crystals, which

[1] Krüss and Ohnmais, *Annalen*, 1891, **263**, 39; Krüss, *Zeit. anory. Chem.*, 1893, **3**, 264; Locke, *Amer. Chem. J.*, 1898, **20**, 373.

[2] Koppel and Berendt, *Zeit. anory. Chem.*, 1903, **35**, 154; Gain, *Compt. rend.*, 1907, **144**, 1157.

become bluish-violet on drying and are very soluble in water, yielding a pure violet-coloured solution, which becomes bluish-violet in the presence of the slightest trace of oxygen. The solution at once reduces copper salts to metallic copper, the reaction proceeding quantitatively according to the equation:

$$2VSO_4 + CuSO_4 = V_2(SO_4)_3 + Cu.$$

The salts of silver, tin, gold, platinum, and mercury are also reduced to the metal.

Vanadious sulphate appears to be isomorphous with ferrous sulphate, $FeSO_4,7H_2O$, and mixed crystals have been obtained both with ferrous sulphate and with magnesium sulphate. It readily forms double salts of the type $R^I_2SO_4,R^{II}SO_4,6H_2O$ with the alkali sulphates. These can be prepared by adding the proper sulphate to the liquid to be reduced and crystallising, &c., as in the preparation of the pure sulphate. The *ammonium* salt, $(NH_4)_2SO_4,VSO_4,6H_2O$, forms reddish-violet monoclinic crystals and is less easily oxidised than the pure sulphate, and the potassium and rubidium salts closely resemble it.[1]

Vanadium Sesquisulphate, $V_2(SO_4)_3$.—When the blue solution of vanadyl sulphate, prepared from 100 grams of vanadic anhydride, 200 c.c. of water and 100 c.c. of concentrated sulphuric acid, is reduced electrolytically until the vanadium is present in the trivalent form, the compound $V_2(SO_4)_3,H_2SO_4,12H_2O$, known as *vanadium sesquisulphate sulphuric acid*, separates out as a green, crystalline powder. It readily forms a salt when evaporated with ammonium sulphate, green crystals separating out of the composition $V_2(SO_4)_3,(NH_4)_2SO_4,12H_2O$.

When the acid is dissolved in a little water, sulphuric acid added, and the mass heated at 180° in a current of carbon dioxide, the anhydrous sulphate separates out as a microcrystalline yellow powder which is insoluble in water.[2] These compounds have a very close resemblance to the corresponding derivatives of titanium sesquioxide (p. 818). A solution of the sulphate acts as a vigorous reducing agent, and precipitates the metal from an acid solution of copper sulphate (Rutter).

Vanadium Alums.—Several alums have been prepared by

[1] Piccini, *Zeit. anorg. Chem.*, 1899, **19**, 204; Piccini and Marino, *Zeit. anorg. Chem.*, 1902, **32**, 55; Marino, *Zeit. anorg. Chem.*, 1906, **50**, 49; Rutter, *Zeit. Elektrochem.*, 1906, **12**, 230; *Zeit. anorg. Chem.*, 1907, **52**, 368.

[2] Stähler and Weithwein, *Ber.*, 1905, **38**, 3978.

treating a metavanadate with sulphurous acid in the presence of sulphuric acid, and then reducing electrolytically. *Ammonium vanadium alum*, $(NH_4)_2SO_4,V_2(SO_4)_3,24H_2O$, crystallises in hemihedral forms of the regular system and is violet-coloured. Alums containing potassium, rubidium, caesium, and thallium have also been prepared.[1] A good yield of the alum is obtained by the electrolysis of ammonium metavanadate. The ammonium metavanadate is placed in a porous cell with 50 per cent. sulphuric acid, a lead cathode being employed. The electrolysis is continued until the solution becomes green, when on standing ammonium vanadium alum crystallises out.[2]

The Vanadyl or Hypovanadic Sulphates.—The blue solution obtained by the action of sulphur dioxide on a suspension of vanadic anhydride in dilute sulphuric acid contains sulphates of the radical $V_2O_2^{IV}$ or VO^{II}. These were termed hypovanadic sulphates by Roscoe, but are now generally known as the vanadyl sulphates. From all solutions in which the molecular ratio $H_2SO_4:VO_2$ is greater than 1·5:1, acid sulphates are obtained up to a temperature of about 201·5°; from solutions in which the ratio is less than this normal salts are obtained, and these are also formed by heating the acid sulphates to about 260°, or by treating them with water or alcohol. At the boiling point of sulphuric acid oxidation occurs, vanadic anhydride and sulphur dioxide being formed (Koppel and Behrendt).

Vanadyl Sulphate, $V_2O_2(SO_4)_2$, is deposited as an insoluble blue sandy powder by dissolving the dioxide, VO_2, in excess of sulphuric acid and heating the solution for some time to 260°.[3] If the dioxide be dissolved in sulphuric acid, the solution evaporated, and the residue treated with absolute alcohol, a sky-blue powder remains, which is a soluble form of the sulphate and deliquesces in moist air. This is also formed by heating the insoluble form with water at 130°. If the solution be allowed to evaporate spontaneously over sulphuric acid, fine blue rhombic prisms having the composition $V_2O_2(SO_4)_2,4H_2O$ are deposited (Berzelius). In addition to this, hydrates with 13, 10, 7, 3, and 2 molecules of water have been described.

When the acid solution containing more than 1·5 molecular

[1] Piccini, *Zeit. anorg. Chem.*, 1896, **11**, 106 *Chem. Centr.*, 1897, i, 223; Bültemann, *Zeit. Elektrochem.*, 1904, **9**, 141.

[2] Renschler, *Zeit. Elektrochem.*, 1912, **18**, 137.

[3] Gerland, *Ber.*, 1877, **10**, 2109; Koppel and Behrendt, *Zeit. anorg. Chem.*, 1903, **35**, 154.

proportions of sulphuric acid is evaporated, various hydrates of the *acid salt* $(V_2O_2)H_2(SO_4)_3$ are obtained. The hydrate with $5H_2O$ is prepared by evaporating the solution on the water bath, and washing the dried crystals with ether (Crow); at 125° the hydrate with $3H_2O$ is formed, and this can also be obtained by precipitating a concentrated solution of any of the vanadyl sulphates with concentrated sulphuric acid. At 150° the dihydrate is formed, at 175° a salt with 0·5 molecule of water, and at 190° the *anhydrous compound*, $2VO_2,3SO_3$, which is a green powder, consisting of microscopic tetragonal tablets, and is sparingly soluble in water (Koppel and Behrendt).[1]

Many double salts also of this series are known; the composition of these compounds will be found in the memoirs cited above.

Normal Divanadyl Trisulphate, $(VO)_2(SO_4)_3$, is obtained, according to Berzelius, by dissolving the pentoxide in hot sulphuric acid which has been diluted with half its weight of water.[2] On evaporating at a low temperature the salt crystallises out in reddish-brown, very deliquescent scales. The same compound is obtained in ruby-red octahedra by boiling the pentoxide with an excess of sulphuric acid. When these are heated to the melting point of lead, the basic salt $(VO)_2O(SO_4)_2$ remains as a red mass, exhibiting small bright crystalline faces.

If the pentoxide be dissolved in concentrated sulphuric acid and the solution evaporated, the basic salt $VO(OH)SO_4$ is formed [3] as a sandy reddish-yellow powder. According to Gerland this is identical with the preceding compound.

When potassium vanadate is dissolved in strong sulphuric acid and the excess of acid driven off by heat, the double salt $K_2SO_4,(VO)_2(SO_4)_3$ is obtained as a yellow crystalline powder (Berzelius).

Vanadium and Nitrogen, Phosphorus, and Arsenic.

425 *Vanadium Mononitride*, VN.—The process described by Berzelius for preparing metallic vanadium by heating the ammonio-oxychloride in an atmosphere of ammonia does not yield the metal, but the mononitride, vanadium being one of

[1] See also Gain, *Compt. rend.*, 1906, **143**, 1154.
[2] See also Ditte, *Compt. rend.*, 1886, **102**, 757.
[3] Gerland, *Ber.*, 1878, **11**, 98.

the metals distinguished by its power of direct union with nitrogen. The substance obtained by strongly igniting the ammonio-oxychloride in a current of dry ammonia (or rather of its component gases) at a white-heat is a greyish-brown powder, which does not undergo change at ordinary temperatures. The mononitride is likewise obtained when the black residue left on calcining ammonium metavanadate in the air is heated to whiteness in a current of dry ammonia. Another and still more simple plan of obtaining the nitride is to expose the oxide to the action of ammonia gas at a white-heat.

When heated in the air vanadium mononitride glows and slowly oxidises to the blue oxide; when heated with soda-lime, ammonia is produced.

Vanadium Dinitride, VN_2, is obtained as a black powder by passing ammonia over vanadyl trichloride, heating the residue in a glass tube to expel ammonium chloride, washing with water, and drying in a vacuum over sulphuric acid.

426 Extended series of phosphovanadic and arsenovanadic acids and their derivatives have been described by Berzelius,[1] Ditte,[2] and Gibbs.[3] According to Friedheim [4] these substances are phosphates and arsenates of vanadium (and double salts of these with the vanadates), in which vanadic anhydride acts as a weak base, the radical VO_2 replacing one or two hydrogen atoms of phosphoric or arsenic acid. They can be prepared by bringing the requisite salts together.

Phosphovanadic Acid, $2(VO_2)H_2PO_4,9H_2O = P_2O_5,V_2O_5,11H_2O$, is formed when vanadic anhydride is heated with syrupy phosphoric acid, and crystallises in golden-yellow flakes.

Arsenovanadic Acid, $As_2O_5,V_2O_5,10H_2O$, is prepared in a similar manner, and forms yellow crystals.

Vanadium and the Elements of the Carbon Group.

427 *Vanadium Carbide*, VC, is formed when vanadic anhydride is heated with carbon in the electric furnace. It forms hard crystals of the specific gravity 5·405, burns in oxygen, and becomes incandescent when heated in chlorine.[5] It is silvery-white, very hard, and melts at 2750°.[6]

[1] *Lehrbuch*, (6) **3**, 1037.
[2] *Compt. rend.*, 1886, **102**, 757
[3] *Amer. Chem. J.*, 1885-6, **7**, 118, 209.
[4] *Ber.*, 1890, **23**, 1530, 2600.
[5] Moissan, *Compt. rend.*, 1896, **122**, 1297.
[6] Ruff and Martin, *Zeit. angew. Chem.*, 1912, **25**, 49.

Vanadium Cyanides. — Double salts of vanadium dicyanide and tricyanide with potassium cyanide of the formulæ $K_4V(CN)_6,3H_2O$ and $K_3V(CN)_6$ have been prepared.[1]

Potassium Vanadic Thiocyanate, $V(SCN)_3,3KSCN,4H_2O$, is prepared in a similar manner to the cyanide (Locke and Edwards), and separates in dark red crystals, the solution of which in water rapidly decomposes. The ammonium and sodium salts have also been obtained.[2]

Complex ammonia vanadyl thiocyanates and oxalates have likewise been prepared.[3]

Vanadium and Silicon.—Vanadium forms two compounds with silicon. The *silicide,* V_2Si, is prepared [4] by heating 120 parts of the sesquioxide with 14 of silicon in the electric furnace, or better by heating this mixture with either carbon or copper. It forms hard, silver-white prisms with a metallic lustre, and has the sp. gr. 5·48 at 17°. It is only attacked by fluorine when gently heated, and it is readily decomposed when heated in chlorine, bromine, or hydrogen chloride. It is insoluble in acids, with the exception of hydrofluoric acid, and is decomposed by fused potash. When it is fused with silicon it is converted into the *disilicide,* VSi_2, which can be obtained also by heating the sesquioxide with an excess of silicon in the electric furnace, or by igniting a mixture of the oxide and silicon with metallic magnesium.[5] It forms hard prisms with a metallic lustre, has the sp. gr. 4·42, and melts and volatilises in the electric furnace. It is soluble in hydrofluoric acid, burns when heated in fluorine, chlorine, or bromine, and is attacked by gaseous hydrogen chloride. It is also decomposed by fused alkalis, and by molten copper, an alloy of this metal with vanadium being formed.

Detection and Estimation of Vanadium.

428 Insoluble vanadium compounds can be brought into solution by treatment either with acids or with alkalis. The hydrochloric acid solution assumes a bright blue colour on the addition of zinc. A solution of vanadyl sulphate cannot be distinguished in colour from one of copper sulphate when diluted

[1] Petersen, *Zeit. anorg. Chem.*, 1904, **38**, 342; Locke and Edwards, *Amer. Chem. J.*, 1898, **20**, 594.

[2] Cioci, *Zeit. anorg. Chem.*, 1899, **19**, 308.

[3] Koppel and Goldmann, *Zeit. anorg. Chem.*, 1903, **36**, 281.

[4] Moissan and Holt, *Compt. rend.*, 1902, **135**, 493.

[5] Moissan and Holt, *Compt. rend.*, 1902, **135**, 78.

to the requisite extent with water. It, however, of course, does not become colourless in presence of metallic iron. Solutions of certain vanadates also closely resemble solutions of the chromates. Thus, for instance, a solution of the tetravanadate of potassium does not differ in appearance from one of potassium dichromate. They may, however, be distinguished from one another, inasmuch as the vanadate solution becomes blue, whilst the chromate assumes a green colour, on reduction. When a solution of vanadic acid or an acid solution of an alkali vanadate is shaken up with ether containing hydrogen peroxide, the aqueous solution assumes a red colour like that of ferric acetate. This reaction serves to detect 1 part of vanadic acid in 40,000 parts of the liquid, and is not affected by the presence of chromic acid.[1]

For the *quantitative* estimation of vanadium, von Hauer proposed the precipitation of ammonium metavanadate, insoluble in solution of ammonium chloride. This on ignition yields the pure pentoxide. This separation of vanadic acid from the metals of the alkalis by means of ammonium chloride, however, gives too low results, both as regards the vanadium and the alkali. It is almost impossible to prevent traces of ammonium metavanadate from dissolving, and on ignition, even with the greatest care, some portions of the finely divided vanadium pentoxide are invariably carried off when the ammonia escapes. On the other hand, the volatilisation of the comparatively large quantities of ammonium chloride which must be employed in order to ensure the complete precipitation of the vanadium almost always entails a considerable loss of the fixed alkali chlorides. A far more accurate plan for the separation of vanadium is the precipitation of the soluble vanadate by lead acetate, when basic lead vanadate is precipitated, which is so insoluble that a portion when finely powdered and boiled in water does not dissolve in sufficient quantity to enable the lead to be detected in the filtrate by the reaction with sulphuretted hydrogen. The salt is insoluble also in acetic acid, but it dissolves readily in nitric acid, liberating vanadic acid, which separates out, but dissolves completely when the liquid is warmed. In the analysis of a soluble vanadate this insoluble lead salt is collected on a filter, dried at 100°, and weighed; a given quantity of the dried salt is then dissolved in nitric acid, the lead precipitated by pure sulphuric acid, and the lead sulphate estimated with the usual

[1] G. Werther, *J. pr. Chem.*, 1863, **88**, 195.

precautions by evaporation, addition of alcohol, &c., or the filtrate is evaporated and the residue heated and weighed as vanadic anhydride.[1] The lead sulphate thus obtained is (contrary to Berzelius's statement) quite free from vanadium, whilst the vanadium pentoxide in the filtrate is obtained perfectly pure and well crystallised on evaporation and ignition. The filtrate from the lead vanadate, freed from excess of lead by means of sulphuric acid and evaporated, yields the alkali sulphate, containing no trace of vanadium. Vanadium may be very readily estimated volumetrically when no other reducible metals are present. For this purpose the solution of vanadic acid in sulphuric acid is diluted and reduced to a vanadyl salt by passing a current of sulphur dioxide through it and afterwards boiling to expel the excess of this gas. Standard permanganate is then added until a permanent coloration is obtained. The inverse process may also be employed, and the acid solution of a vanadate titrated with decinormal ferrous sulphate solution, potassium ferricyanide being employed as indicator.[2] Under these circumstances the acid is reduced to VO_2 and the process can be carried out in the presence of copper. The reduction may also be effected by repeated evaporation with hydrochloric acid.[3]

The Atomic Weight of vanadium has been determined in several ways. One is by igniting vanadium pentoxide in dry hydrogen, when it is reduced to the sesquioxide, and the atomic weight of vanadium is then deduced by the relation,

$$\frac{a}{b} = \frac{2x + 5 \times 16{\cdot}00}{2x + 3 \times 16{\cdot}00}, \text{ whence } x = 8{\cdot}00\,\frac{(5b - 3a)}{a - b},$$

where a is the weight of vanadium pentoxide taken, and b is the weight of sesquioxide obtained.

The following results were obtained by Roscoe:[4]

	Weight of pentoxide taken.	Weight of sesquioxide obtained.	Atomic weight of vanadium.
(1) . .	7·7397	6·3827	51·26
(2) . .	6·5819	5·4296	51·39
(3) . .	5·1895	4·2819	51·49
(4) . .	5·0450	4·1614	51·35

[1] Cormimbœuf, *Ann. Chim. anal.*, 1902, **7**, 258.

[2] Williams, *J. Soc. Chem. Ind.*, 1902, **21**, 389.

[3] Campagne, *Ber.*, 1903, **36**, 3164; see also Gooch and Stookey, *Amer. J. Sci.*, 1902, [4], **14**, 369; Gooch and Gilbert, *Zeit. anorg. Chem.*, 1903, **35**, 420.

[4] *Phil. Trans.*, 1868, **158**, 6.

The mean atomic weight of these four experiments is 51·37. A second and more reliable method for the determination of the atomic weight of vanadium is the analysis of vanadyl trichloride. The chlorine in this compound was estimated by Roscoe both volumetrically and gravimetrically. Nine volumetric determinations gave for the ratio $VOCl_3 : Ag$ the mean value 53·59 : 100, while eight gravimetric estimations gave for the ratio $VOCl_3 : AgCl$ the mean value 40·38 : 100. The atomic weight deduced from the mean of both series is 51·16. A more recent gravimetric analysis of vanadyl trichloride by Prandtl and Bleyer [1] has given the value 51·06, while McAdam,[2] by the reduction of sodium vanadate to sodium chloride, finds 50·97. The value now (1913) adopted for the atomic weight of vanadium is 51·0.

COLUMBIUM (Niobium). Cb = 93·5.

429 This metal is so closely connected with the next member of the same group, tantalum, that it will be most convenient to consider their history together.

In the year 1801, Hatchett[1] laid before the Royal Society an investigation on a mineral known as columbite, from Massachusetts, which he believed to contain a new metal to which he gave the name of *columbium*. In the following year, Ekeberg,[2] in Sweden, investigating the yttrium minerals, discovered a new element in a mineral to which he afterwards gave the name of yttrotantalite, whilst the same element also occurred in a mineral termed tantalite. In consequence of this he named the metal *tantalum*, partly because mythological names were frequently used, and partly also as pointing to the fact "that when placed in the midst of acids it is incapable of taking any of them up and saturating itself with them."

In 1809, Wollaston [3] endeavoured to show that columbium and tantalum were identical, and a few years later Berzelius [4] more carefully investigated the oxides of the last-named metal obtained from tantalite, and prepared tantalic acid. After-

[1] *Zeit. anorg. Chem.*, 1909, **65**, 152; 1910, **67**, 257.
[2] *J. Amer. Chem. Soc.*, 1910, **32**, 1603.
[3] *Phil. Trans.*, 1802, **92**, 49.
[4] *Ann. Chim.*, 1802, **43**, 276.
[5] *Phil. Trans.*, 1809, **99**, 246.
[6] *Pogg. Ann.*, 1820, **4**, 6.

wards, in 1839, Wöhler[1] found that the acid-forming oxide contained in pyrochlor and in the Bavarian tantalites possessed peculiar properties; and Rose[2] then observed that the columbites of Bodenmais contained the oxide of a new metal, to which he gave the name of niobium (Nb), and in 1846 he thought that he had found a third new metal, to which he gave the name of *pelopium*. In 1853 he came to the conclusion on further investigation that niobic acid and pelopic acid were different oxides of niobium, and to the first of these he gave the name of niobic acid, whilst the latter was designated as hyponiobic acid. These, however, exhibited "a relationship so peculiar that the whole range of chemistry does not furnish an example of a similar kind."[3] In 1856–7 Hermann observed that niobium and tantalum usually occurred together, whilst in 1864–5, Blomstrand[4] showed that Rose's hyponiobic chloride contained oxygen, and was an oxychloride, and Marignac[5] almost at the same time proved that the double salts which hyponiobic fluoride forms with metallic fluorides are isomorphous with similar double salts containing titanium fluoride, TiF_4, and tungsten oxyfluoride, WO_2F_2. Inasmuch as the sum of the atoms in all these isomorphous compounds is constant, and as, according to analysis, the hyponiobic fluoride contains three atoms of fluorine for one of oxygen, Marignac concluded that it must be an oxyfluoride of the composition $NbOF_3$, and he succeeded in obtaining experimental evidence of the truth of this view. At the same time he showed that tantalic acid, which up to that time had been supposed to be analogous to titanic acid, and to which the formula TaO_2 had been given, must, like the highest oxide of niobium, be a pentoxide, as these two oxides occur in isomorphous mixture in several minerals, and as both metals form isomorphous double fluorides, such as K_2TaF_7 and K_2NbF_7.

The name columbium, originally proposed by Hatchett, has always been employed in America for Rose's niobium, and has recently also been adopted in England, whilst in Germany the name niobium is retained.

The truth of this view of the composition of the columbium and tantalum compounds was confirmed by the experiments of Deville and Troost,[6] who in 1865 determined the vapour

[1] *Pogg. Ann.*, 1839, **48**, 91.
[2] *Pogg. Ann.*, 1844, **63**, 307, 693; 1846, **69**, 118.
[3] *Pogg. Ann.*, 1853, **90**, 471. [4] *J. pr. Chem.*, 1866, **97**, 37.
[5] *Ann. Chim. Phys.*, 1866, [4], **8**, 5, 49.
[6] *Compt. rend.*, 1865, **60**, 1221.

densities of columbium chloride, columbium oxychloride, and tantalum chloride, which were found to correspond to the formulæ $CbCl_5$, $CbOCl_3$, and $TaCl_5$. The investigations of Blomstrand and Marignac next showed that the metal *dianium*, supposed by v. Kobell to be contained in various columbites, is in fact identical with columbium, and Marignac further showed that *ilmenium*, which Hermann believed he had discovered in samarskite, is a mixture of columbium and tantalum. It appears certain that *neptunium*, also discovered by Hermann, is a similar mixture.[1]

430 Columbium and tantalum are found in many other minerals in addition to those already mentioned. The following tables give the composition of some of the more important of these.

Mineral.	Columbite.		Tantalite.	
Analyst.	Blomstrand.		Rammelsberg.	
Locality	Green-land.	Massa-chusetts.	Finland.	Sweden.
Ta_2O_5	—	28·55	76·34	49·64
Cb_2O_5	77·97	51·53	7·54	29·27
WO_3	0·13	0·76	—	—
SnO_2	0·73	0·34	0·70	2·49
FeO	17·33	13·54	13·90	13·77
MnO	3·28	4·55	1·42	2·88
ZrO_2	0·13	0·34	—	—
MgO	0·23	0·42	—	—
PbO	0·12	—	—	—
H_2O	—	0·16	—	—
	99·92	100·19	99·90	98·05

[1] See Smith, *Proc. Amer. Phil. Soc.*, 1905, **44**, 151.

Pyrochlor (*analysed by Rammelsberg*).

Locality	Siberia.	Kaiserstuhl.
Cb_2O_5	53·19	47·13
TiO_2	10·47	13·52
ThO_2	7·56	—
Ce_2O_3	7·00	7·30
CaO	14·21	15·94
MgO	0·22	0·19
FeO	1·84	10·03
Na_2O	3·71	3·12
F	3·06	2·90
	101·26	100·13

Yttrotantalite, Fergusonite, Euxenite (*analysed by Rammelsberg*).

	Yttrotantalite.	Fergusonite.	Euxenite.
Locality	Ytterby.	Greenland.	Arendal.
Ta_2O_5	10·05	6·30	—
Cb_2O_5	42·12	44·45	35·83
WO_3	0·22	0·15	—
SnO_2	0·24	0·47	24·33
Yt_2O_3	27·69	24·87	17·23
Er_2O_3	12·44	9·81	9·39
Ce_2O_3	1·90	2·00	2·34
CaO	3·21	0·61	—
FeO	0·63	0·74	3·61
UO_2	1·26	2·58	8·86
La_2O_3	—	5·63	—
H_2O	—	1·49	—
	99·76	99·10	101·59

Besides occurring in these minerals, columbium and tantalum are frequently found in small quantities in tinstone, wolfram, pitchblende, and other minerals.

For the purpose of preparing the columbium and tantalum compounds, tantalite, fergusonite, or some other mineral containing these metals, is finely powdered and fused with three times its weight of acid potassium sulphate; the fused mass is completely boiled out with water, and the residue digested with ammonium sulphide in order to remove tin and tungsten, the iron present being at the same time converted into sulphide. The residue is washed and boiled with dilute hydrochloric acid, when the hydroxides of columbium and tantalum, together with titanic acid and silica, remain behind, and are then well washed with boiling water. The mass is dissolved in hydrofluoric acid, filtered from any residue, and heated to remove silicon fluoride. Titanium, columbium, and tantalum are then separated by the different solubilities of their double potassium fluorides. To the boiling hydrofluoric acid solution 1 part of potassium fluoride is added for every 4 parts of oxide present, and the solution concentrated until 1 gram of oxide is contained in 7 c.c. of the solution. On cooling, fine needle-shaped crystals of potassium tantalofluoride separate out, mixed with titanofluoride. These are washed with water until the wash-water after standing for two hours does not give an orange-red precipitate, but a sulphur-yellow one, with tincture of galls. On evaporating the mother-liquor and the wash-water, more of the salt is obtained, which at last is mixed with scales of the columbium salt. The potassium tantalofluoride purified by recrystallisation is then mixed with its own weight of concentrated sulphuric acid and heated gradually to 400°, and the residue boiled out with water, when a granular crystalline compound of tantalum oxide and sulphuric acid remains behind. This is decomposed by ignition, and it is advisable to add ammonium carbonate in order to get rid of the whole of the sulphuric acid.

The filtrate from the tantalum salt deposits the compound $2KF,CbOF_3,H_2O$ when it is concentrated, and from this the columbic oxide may be prepared by decomposition with sulphuric acid and washing or continued boiling with water. The double fluoride thus obtained is not always pure, but may be purified by repeatedly boiling with water, and reconverting the white deposit, which has the formula $2KF,3CbO_2F$, into the normal oxyfluoride by treatment with hydrofluoric acid and potassium fluoride.[1]

The last traces of tantalum may be removed from oxide of

[1] Krüss and Nilson, *Ber.*, 1887, **20**, 1676.

columbium by converting the mixture into the potassium oxyfluoride, heating at 150–175°, and treating with water. The tantalum remains as an insoluble residue, and by a repetition of the process may be completely removed. Titanium is also difficult to separate completely from columbium, and is best removed by repeated precipitation of a solution of the oxyfluoride with ammonia, the titanium remaining in solution.[1]

The minerals may also be brought into solution by fusion with acid potassium fluoride, this process being specially suitable for columbite (Gibbs).

431 Columbium was first obtained by Blomstrand,[2] by reducing the chloride in hydrogen, as a mirror-like deposit on the tube, but it was not certain whether this was the pure metal or a hydride. Roscoe[3] obtained it in the form of a steel-grey crust, by passing the vapour of the pure chloride together with hydrogen repeatedly through a red-hot tube; this was then more strongly heated in a porcelain tube, through which hydrogen was passed. The metal contained only 0·27 per cent. of hydrogen as well as a small quantity of chloride and oxide, the latter being derived from diffused air. It has been prepared in a somewhat impure condition as a metallic regulus by heating the pentoxide with carbon in the electric furnace,[4] and by reducing the pentoxide with the mixed metals of the cerite earths, the method being the same as that employed for vanadium (p. 916).[5] It can be obtained in the pure condition by preparing filaments of the oxide CbO_2, by heating a mixture of the pentoxide and paraffin which has been pressed into threads, and then reducing this by passing through it an alternating current in vacuo. The regulus obtained by the aluminium reduction of the pentoxide may moreover be freed from aluminium by being heated in vacuo in an electric furnace.[6] The metal has the specific heat 0·071 and the density 8·4, and melts at about 1950°. The pure metal has a light grey colour, and is about as hard as wrought iron. It can be rolled into foil and then drawn into wire, and can be welded at a red heat. A regulus fused in vacuum consists of crystals, apparently

[1] Hall, *J. Amer. Chem. Soc.*, 1904, **26**, 1235. See also Smith, *Proc. Amer. Phil. Soc.*, 1905, **44**, 151, 177.

[2] *J. pr. Chem.*, 1866, **97**, 37.

[3] *Mem. Manch. Phil. Soc.*, [3], 6, 186.

[4] Moissan, *Compt. rend.*, 1901, **133**, 20.

[5] Weiss and Aichel, *Annalen*, 1904, **337**, 380.

[6] Werner von Bolton, *Zeit. Elektrochem.*, 1907, **13**, 145.

rhombic, several mm. in length. It combines only slowly with oxygen, even when it is strongly heated, and unites with hydrogen to form the hydride, CbH. This compound, which has also been obtained by Marignac, resembles the metal in its behaviour to acids, and burns when heated in the air.[1] Columbium is not dissolved by hydrochloric or nitric acid or aqua regia, even when heated, but when alloyed with other metals is attacked by acids. It is attacked by fused alkalis and fused oxidising agents, and combines with nitrogen at 1200°.

COMPOUNDS OF COLUMBIUM.

Columbium and Oxygen.

432 The two lower oxides of columbium are usually known as the dioxide, Cb_2O_2, and the tetroxide, Cb_2O_4, although they would more properly be termed the monoxide, CbO, and the dioxide, CbO_2.

Columbium Dioxide, CbO or Cb_2O_2, is formed when dry potassium columbium oxyfluoride is heated with sodium under a layer of potassium chloride over a gas blow-pipe, and was thought by Rose to be the metal. The fused mass is boiled with water, and the residue washed with water and afterwards with dilute alcohol. It then forms a white powder which on heating in the air oxidises with vivid incandescence. When gently warmed in chlorine gas it burns with formation of oxychloride, and it dissolves in the moist state in hydrochloric acid with evolution of hydrogen. If the vapour of the oxychloride be passed over heated magnesium wire, the same compound is formed in crystals which belong probably to the regular system.

Columbium Tetroxide, CbO_2 or Cb_2O_4, is obtained as a heavy black powder, which appears blue by reflected light, by heating the pentoxide very strongly in hydrogen or with metallic magnesium.[2] It is not attacked by acids, and burns in the air when heated to redness.

Columbium Pentoxide, Cb_2O_5, is best prepared from Greenland columbite which, as already mentioned, is converted into potassium columboxyfluoride; this is purified by repeated crystallisation, and then decomposed with sulphuric acid and the solution

[1] Krüss and Nilson, *Ber.*, 1887, **20**, 1691.
[2] Smith and Maas, *Zeit. anorg. Chem.*, 1894, **7**, 96.

boiled with water. It is a white amorphous infusible powder having a sp. gr. of 4·53, and becomes crystalline when strongly heated. It may be obtained in prismatic crystals of sp. gr. 4·568 by fusion with boron trioxide or borax.

Columbic Acid or *Columbium Hydroxide*, $HCbO_3$, is formed by the decomposition of the oxychloride or pentachloride in moist air or with water. It is a white powder which, when dried at 100°, retains varying quantities of water, and is converted into the pentoxide at a red heat with incandescence. It is only slightly soluble in hot hydrochloric acid, but the residue, after this treatment, can be dissolved in water. On the addition of zinc the solution becomes blue and a hydrated precipitate, probably of Cb_2O_4, separates out. The solution of columbic acid obtained by treatment with hydrochloric acid gives, on the other hand, a brown colour with zinc, and a brown oxide separates out which has the composition $Cb_3O_5 (= CbO,2CbO_2)$. Columbic acid is easily soluble in caustic alkalis and their carbonates.

Potassium Hexacolumbate, $K_8Cb_6O_{19},16H_2O$, is prepared by fusing the pentoxide with double its weight of potassium carbonate, dissolving in water, and evaporating in a vacuum. It forms large glistening monoclinic crystals which effloresce on exposure to air. If caustic potash be added to this solution and the mixture slowly evaporated, fine rhombic pyramids of $K_6Cb_4O_{13},13H_2O$ are deposited, and these effloresce quickly on exposure.[1]

When equal molecular proportions of columbium pentoxide and potassium carbonate are fused together a distinctly crystalline mass is obtained, which, when treated with water, yields the salt $2K_2Cb_4O_{11},11H_2O$. If, however, a larger quantity of potassium carbonate be employed, the compound $K_4Cb_2O_7,11H_2O$ is obtained.[2]

Rose described a number of crystalline sodium columbates, the individuality of which was doubted by Marignac, and it has been found by Bedford[3] that the only definite compound obtainable by Rose's method is a salt of the composition $7Na_2O,6Cb_2O_5,32H_2O$. The columbates of the metals of the other groups have been prepared by Joly and correspond closely to the tantalates.

[1] Marignac, *Ann. Chim. Phys.*, 1866, [4], **8**, 20.
[2] Santesson, *Bull. Soc. chim.*, 1875, [2], **24**, 53.
[3] Bedford, *J. Amer. Chem. Soc.*, 1904, **26**, 1235.

Numerous crystalline columbates have been prepared by fusing the precipitated salts with the corresponding chlorides or with boric acid.[1]

When the oxide is fused with sodium fluoride, compounds resembling various minerals in composition are obtained.[2]

Percolumbic Acid is formed as an amorphous yellow powder when columbic acid is warmed with hydrogen peroxide, or when sulphuric acid is added to a solution of potassium percolumbate and the solution dialysed and evaporated.[3] It has the composition of a hydrated percolumbic acid, $HCbO_4$, and is decomposed by dilute sulphuric acid only on warming, thus differing from other per-acids. The *potassium salt*, $K_4Cb_2O_{11},3H_2O$, which may be regarded as derived from a pyropercolumbic acid, is prepared by adding hydrogen peroxide to a solution of potassium columbate and precipitating with alcohol. It is slowly decomposed by water, and yields hydrogen peroxide with dilute sulphuric acid, and ozonised oxygen with concentrated sulphuric acid.

Orthopercolumbates of the general formula M_3CbO_8, where M is a univalent metal, have also been obtained;[4] these represent some of the most highly oxidised series of salts known.

Columbium and the Halogens.

433 *Columbium Pentafluoride*, CbF_5.—This substance, like tantalum fluoride, is known only in solution, and possesses analogous properties to the latter compound.

Columbium Oxyfluoride, $CbOF_3$, is obtained by igniting a mixture of pentoxide and fluor-spar in a current of hydrogen chloride, in the form of small crystals closely resembling zirconium fluoride. It forms double salts with other metallic fluorides, of which those of potassium and ammonium have been investigated by Marignac, who prepared the following:

$2KF,CbOF_3,H_2O$	$2NH_4F,CbOF_3$
$3KF,CbOF_3$	$3NH_4F,CbOF_3$
$5KF,3CbOF_3,H_2O$	$5NH_4F,3CbOF_3,H_2O$
$4KF,3CbOF_3,2H_2O$	$NH_4F,CbOF_3$
$HF,3KF,CbOF_3$	$3NH_4F,CbOF_3,CbF_5$

[1] Larsson, *Zeit. anorg. Chem.*, 1896, **12**, 188.

[2] Holmquist, *Journ. Chem. Soc.* 1898, **74**, ii, 388.

[3] Melikoff and Pissarjewsky, *Zeit. anorg. Chem.*, 1899, **20**, 340. See also Hall and Smith, *Proc. Amer. Phil. Soc.*, 1906, **44**, 177.

[4] Balke and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1637.

These are crystallisable, and are formed by dissolving columbic acid in a larger or smaller quantity of hydrofluoric acid and adding the other fluorides in various proportions. The first salts of the two series, which Marignac terms normal salts, are those which are readily formed. The normal potassium salt is formed whenever the others are recrystallised, and is deposited in the form of thin monoclinic scales isomorphous with potassium tungsten oxyfluoride, $2KF,WO_2F_2$, and with potassium titanofluoride, K_2TiF_6. By dissolving this in hot hydrofluoric acid *potassium columbifluoride.* K_2CbF_7, is formed, which is deposited in glistening rhombic needles. The normal ammonium salt crystallises in rhombic tablets, and is isomorphous with ammonium tungsten oxyfluoride, $2NH_4F,WO_2F_2$.

A double fluoride of the formula $2KF,3CbO_2F$ is gradually deposited in small quantity as a white powder when a solution of the normal potassium oxyfluoride is boiled for a considerable time:[1]

$$3(2KF,CbOF_3)+3H_2O=2KF,3CbO_2F+4KF+6HF.$$

It is readily soluble in hydrofluoric acid.

Hydrogen peroxide converts the oxyfluoride into a peroxyfluoride, CbO_2F_3, which crystallises in yellowish plates.[2]

Columbium Trichloride, $CbCl_3$, is obtained when the vapour of the pentachloride is slowly passed through a red-hot glass tube, and when the oxide is heated with phosphorus pentachloride.[3] It either forms crystalline crusts which have the appearance of iodine, or is found crystallised in long needles which are dichroic. It is neither volatile nor deliquescent, and is not decomposed by water or ammonia, but is easily oxidised by nitric acid. When heated in the air it emits thick vapours, and when ignited in a current of carbon dioxide it forms columbium oxychloride, $CbOCl_3$, and carbon monoxide, a reaction which is not exhibited by any other metallic chloride (Roscoe).

Columbium Pentachloride, $CbCl_5$.—When an intimate mixture of columbium pentoxide and a large excess of sugar charcoal is heated in a current of chlorine perfectly free from air, yellow needles of the above compound are formed. The chloride is also formed[4] when the pentoxide is heated with sulphur

[1] Krüss and Nilson, *Ber.*, 1887, **20**, 1676.

[2] Piccini, *Zeit. anorg. Chem.*, 1892, **2**, 22.

[3] Pennington, *Chem. News*, 1897, **75**, 38.

[4] Smith, *J. Amer. Chem. Soc.*, 1898, **20**, 289; *Proc. Amer. Phil. Soc.*, 1905, **44**, 177; Hall, *J. Amer. Chem. Soc.*, 1904, **26**, 1235.

monochloride, S_2Cl_2, or carbon tetrachloride in a sealed tube at 200°, and together with a large amount of the oxychloride when carbon tetrachloride is passed over the heated pentoxide.[1] It melts at 194°, and boils at 240·5°, but begins to sublime at 125°. The yellow vapour has a specific gravity of 9·6 (Deville and Troost), the formula requiring 9·38. The chloride is soluble in carbon tetrachloride, sulphur monochloride, chloroform, and alcohol. It dissolves in hydrochloric acid, forming a liquid which gelatinises on standing, and when diluted with water or boiled almost all the columbic acid separates out. Metallic zinc brought into the solution turns it a deep blue colour.

Columbium Oxychloride, or *Columbyl Chloride*, $CbOCl_3$, is formed by the direct union of the dioxide with chlorine, and also when a mixture of the pentoxide with a small quantity of carbon is heated in chlorine. It is likewise formed by repeatedly distilling the pentachloride in a current of carbon dioxide over ignited pentoxide. It is a colourless, fibrous, crystalline mass, which volatilises without melting at about 400°, giving rise to a colourless vapour, the specific gravity of which was determined by Deville and Troost to be 7·88, theory requiring 7·48. When heated in carbon dioxide, and still more readily in hydrogen, it decomposes into pentoxide and pentachloride. It deliquesces on exposure to moist air, with formation of crystalline columbic acid, whilst when brought into contact with water it decomposes violently, forming amorphous columbic acid.

Double salts with various alkali chlorides and organic hydrochlorides have been prepared.[2]

When columbium oxide is heated in hydrogen chloride a hydroxychloride, $Cb_2O_4,3H_2O,HCl$, is formed which is volatile at a high temperature.[3] Hydrogen bromide yields an analogous compound.

Columbium Pentabromide, $CbBr_5$, is prepared in the same way as the chloride, and is a purple-red mass, which on heating becomes yellow and volatilises.

Columbium Oxybromide, $CbOBr_3$.—When a mixture of the pentoxide and double its weight of carbon is heated in bromine vapour a yellow voluminous mass of the oxybromide is obtained, which sublimes without fusion, and when heated in carbon dioxide is reconverted into the pentoxide.

[1] Delafontaine and Linebarger, *J. Amer. Chem. Soc.*, 1896, **18**, 532.
[2] Weinland and Storz, *Ber.*, 1906, **39**, 3056; *Zeit. anorg. Chem.*, 1907, **54**, 223.
[3] Smith and Maas, *Zeit. anorg. Chem.*, 1894, **7**, 96.

Columbium and Sulphur.

434 *Columbium Oxysulphide,* $CbOS_3$, is formed when carbon dioxide mixed with the vapour of carbon disulphide is passed over the white-hot pentoxide. It is a black or brass-coloured crystalline powder. The same compound is easily obtained, as a black woolly mass, by heating the oxychloride in sulphuretted hydrogen. This powder, when rubbed in an agate mortar, attains a steely lustre, and when heated burns in the air with formation of pentoxide.

Columbium and Nitrogen.

435 *Columbium Nitride,* Cb_3N_5.—Metallic columbium forms a yellow nitride[1] when it is heated in nitrogen at 1,200°. When columbium pentoxide is heated to whiteness in ammonia it loses the half of its oxygen and forms a black powder containing nitrogen. If the oxychloride be treated with dry ammonia it becomes hot and turns yellow. This mass, when heated, gives off ammonium chloride, and a black powder remains behind, which, when melted with caustic potash, yields ammonia in large quantity, and on heating in the air burns with incandescence. It is not attacked either by boiling nitric acid or aqua regia, but dissolves readily in a mixture of hydrofluoric and nitric acids.

Detection and Estimation of Columbium.

436 The solution of a columbate yields with potassium ferrocyanide and hydrochloric acid a deep brown precipitate. Under some circumstances tincture of galls or tannic acid gives an orange-red precipitate. When zinc is added to the acidified solution the whole becomes blue and afterwards brown. In the presence of potassium thiocyanate, zinc and hydrochloric acid produce a bright golden brown coloration. Microcosmic salt or borax easily dissolves the pentoxide, and a bead is obtained which becomes violet, blue, or brown in the reducing flame and red on the addition of ferric oxide.

The *quantitative* estimation and separation of columbium is best understood from the following description of Rose's method,

[1] Moissan, *Compt. rend.*, 1901, **133**, 20; Muthman, Weiss and Riedelbauch, *Annalen*, 1907, **355**, 58.

given by Rammelsberg, for the analysis of tantalites and columbites.[1] The mixture of oxides obtained by fusion with acid potassium sulphate and lixiviation with water is fused with sulphur and sodium carbonate, and the fused mass treated with water, when any tin sulphide or tungsten sulphide which may be present is dissolved. The residual oxides of tantalum and columbium are then treated with dilute sulphuric acid in order to remove the iron, and again fused with acid potassium sulphate, and the oxides separated out by boiling the mass with water, whilst any iron, manganese, zinc, copper, or tin which may still be present is found in solution.

In order to separate columbium from tantalum the purified oxides are fused with potassium fluoride, the mass digested with a large quantity of water, and the solution boiled after addition of some hydrofluoric acid. On cooling, the largest portion of the tantalum separates out, chiefly as tantalofluoride. The filtrate is evaporated to two-thirds of its bulk, allowed to stand twenty-four hours in the cold, when the rest of the salt is obtained. Sometimes, however, a third evaporation of the filtrate is necessary. The potassium tantalofluoride can then be weighed, but it generally contains some iron which must be separated by heating with sulphuric acid, the purified tantalum being weighed as the pentoxide.

The solution which contains the columbium is also evaporated with sulphuric acid, the residue ignited and well washed with water, and again ignited, when columbium pentoxide remains behind. This may still contain a trace of titanium. In order to free it from this metal the fluo-double-salts are warmed with hydrochloric acid and zinc, when the titanium compound is reduced, and its amount estimated by volumetric analysis with potassium permanganate.

The Atomic Weight of columbium was determined by Marignac[2] to be 94 from numerous analyses of potassium columbium oxyfluoride and columbium pentachloride. Balke and Smith[3] have made a determination of the atomic weight of columbium based on the ratio between the chloride and oxide, and find the mean value 93·50. The number now adopted (1913) is 93·5.

[1] *Pogg. Ann.*, 1872, **146**, 56.
[2] *Ann. Chim. Phys.*, 1866, [4], **8**, 16.
[3] *J. Amer. Chem. Soc*, 1908, **30**, 1637.

TANTALUM. Ta = 181·5.

437 Metallic tantalum was first obtained in an impure state as a black powder by Berzelius, who heated potassium tantalofluoride with potassium. Moissan succeeded in preparing it as a fused regulus by reducing the pentoxide with carbon in the electric furnace, but the metal thus obtained contained carbon.[1] It was first obtained pure by von Bolton,[2] who prepared it by carrying out Berzelius's reaction, and then heating the compressed powder of the metal in an electric furnace in a vacuum, and also by passing a current through a filament of Ta_2O_4 in a vacuum, the oxygen being thus removed and a filament of the metal left. It is also formed when the pentoxide is reduced by crude cerium (Weiss and Aichel), but the temperature is not sufficiently high to melt the tantalum, which is obtained as a silver-white porous mass. It is now manufactured by the action of sodium on sodium tantalofluoride.[3]

The pure metal is silver-white in colour, has the sp. gr. 16·64 (von Bolton), melts at 2,850 (Pirani and Meyer), and has a normal atomic heat. It is as hard as the best steel, and when hot can be rolled, hammered, and drawn into wire. The tensile strength of the metal is very high, a fine wire giving a breaking test of 93 kilograms per square mm.

When heated in the air, thin wire burns, whilst more compact masses are oxidised superficially. The red-hot powder decomposes water, and the metal in the form of wire readily absorbs hydrogen, 740 volumes being taken up at a yellow heat. About three-quarters of this is lost in a vacuum at a red heat, but the remainder, which renders the metal brittle and increases its electrical resistance, is lost only on fusion.[4] Tantalum is not attacked by aqua regia nor by any single acid except hydrofluoric acid, which dissolves it much more readily when the metal is in contact with platinum. It is attacked also by fused alkalis. It combines with nitrogen at a high temperature, more readily with sulphur. Carbon appears to form with it a carbide and renders

[1] *Compt. rend.*, 1902, **134**, 211.

[2] *Zeit. Elektrochem.*, 1905, **11**, 45, 503, 722; German Patents, 152848; 152870; 153826; 155548; 161081; 163414; 171562.

[3] *Mining Journal*, 1906, **80**, 363.

[4] Piccini, *Zeit. Elektrochem.*, 1905, **11**, 555.

the metal brittle. Alloys with iron, tungsten, and molybdenum can be obtained.

The chief purpose for which metallic tantalum is employed is for the preparation of filaments for electric lamps. Wire of 0·05 mm. diameter is employed and as the resistance is much less than that of a carbon filament, a much longer filament is used than in a carbon lamp. The lamps require only about half the electrical energy needed by a carbon lamp of equal candle power.

It has recently been suggested to use tantalum in place of the more expensive platinum. It can be used in place of platinum for electrodes and for dental and surgical instruments.

COMPOUNDS OF TANTALUM.

Tantalum and Oxygen.

438 *Tantalum Tetroxide*, Ta_2O_4 or TaO_2, is formed when the pentoxide is heated in a very small carbon crucible, exposed to the highest heat of a wind furnace, or reduced by metallic magnesium. It is a porous dark-grey mass which scratches glass, and when rubbed on a hone has a steel-grey colour. It gives a dark-brown non-metallic powder, and is not attacked by acids, even by a mixture of hydrofluoric and nitric acids, but burns when heated, with formation of the pentoxide.

Tantalum Pentoxide, Ta_2O_5.—The preparation of this body has already been described (p. 948). It is a white amorphous infusible powder which when strongly heated becomes crystalline, and when ignited with boron trioxide or melted with microcosmic salt in a porcelain furnace is obtained in rhombic prisms. When gently heated it has a specific gravity of 7·35, which after exposure to a white heat rises to 8·01. The ignited pentoxide does not dissolve in any acid, but volatilises completely when ignited with ammonium fluoride.

Tantalic Acid or *Tantalum Hydroxide*, $HTaO_3$, is obtained in the form of a gelatinous mass when the chloride is quickly mixed with water. If, however, the same compound be exposed to moist air until it is decomposed, and then mixed with water containing ammonia, the hydroxide is obtained as a crystalline powder, which when dried at 100° possesses the above composition, and is converted with vivid incandescence into pentoxide when heated to low redness. The hydroxide obtained by ignition

with acid potassium sulphate does not exhibit this phenomenon. Tantalic acid dissolves in binoxalate of potash, in hydrofluoric acid, and, when freshly precipitated, in other acids.

The Tantalates.—The normal tantalates, to which class the tantalum minerals belong, are all insoluble in water. Besides these, others are known, derived from the unknown hydrate, hexatantalic acid, $H_8Ta_6O_{19}$, of which only the compounds of the alkali metals are soluble in water.

Potassium Hexatantalate, $K_8Ta_6O_{19},16H_2O$, is formed by dissolving the acid in caustic potash, and also by fusing the pentoxide with double its weight of caustic potash. The fused mass is dissolved in water and allowed to evaporate in a vacuum. Transparent glistening monoclinic crystals are thus obtained which dissolve in lukewarm water without decomposition. On boiling or evaporating in the air, salts containing more tantalum are formed. If it be repeatedly ignited with ammonium chloride and washed with water the normal salt $KTaO_3$ is obtained.

Sodium Hexatantalate, $Na_8Ta_6O_{19},25H_2O$, is obtained in a similar way to the potassium salt, a vivid incandescence occurring when the mixture is heated to redness. The fused mass is boiled out with water, and the solution either allowed to cool or, inasmuch as the salt is insoluble in caustic soda, poured on to the top of a strong solution of this substance. It crystallises in small hexagonal tablets which dissolve at 13·5° in 493, and at 100° in 162 parts of water. It is not decomposed by boiling water, and if the aqueous solution be mixed with alcohol a precipitate of $NaTaO_3,H_2O$ is formed, and this becomes anhydrous on ignition. The anhydrous salt is also formed by the ignition of the hexatantalate.

Ammonium Tritantalate is produced by the addition of ammonium chloride to a solution of the sodium salt, and is a precipitate which resembles chloride of silver, and is slightly soluble in water. Its composition is uncertain.

When tantalum pentoxide is strongly ignited with the chlorides of calcium, magnesium, and other metals, crystalline tantalates of these metals are obtained.[1]

Pertantalic Acid.—When a large excess of hydrogen peroxide is added to a solution of potassium hexatantalate and the liquid mixed with an equal volume of alcohol, a white crystalline precipitate of *potassium pertantalate*, $K_3TaO_8,\frac{1}{2}H_2O$,

[1] Joly, *Compt. rend.*, 1875 **81**, 266, 1266.

is obtained.[1] This salt is decomposed by sulphuric acid with formation of a white precipitate of hydrated *pertantalic acid*, $HTaO_4$. This substance is more stable than percolumbic acid, but yields hydrogen peroxide when heated for some time at 100° with dilute sulphuric acid, and evolves ozonised oxygen when treated with concentrated sulphuric acid. The salts appear to be derived from the unknown ortho-form of this acid, which would have the formula $(HO{\cdot}O)_3TaO_2$.

Tantalum and the Halogens.

439 *Tantalum Pentafluoride*, TaF_5, is known only in solution. If this be evaporated, even at a moderate temperature, some of the fluorine volatilises, whilst tantalic acid remains behind. Tantalum fluoride forms double salts with the other metallic fluorides.

Potassium Tantalofluoride, K_2TaF_7.—The mode of preparing this salt has been already described (p. 948). It forms small rhombic needles which readily melt, but it does not decompose when ignited even to whiteness in a platinum vessel. It is easily soluble in hot, though sparingly so in cold water. When the solution is boiled decomposition takes place rapidly, a white powder of the *oxyfluoride*, $K_4Ta_4O_5F_{14} = 4KF,2TaF_5,Ta_2O_5$, separating out. This reaction serves to detect the smallest quantity of tantalum when present together with columbium oxyfluoride (Marignac).

Sodium Tantalofluoride, Na_2TaF_7,H_2O, is obtained in a similar manner to the potassium salt, or by dissolving sodium hexatantalate in hydrofluoric acid. On evaporation indistinct crystals of Na_3TaF_8 separate out, and then eight-sided rhombic tablets of the above salt, which lose their water under 100°.

Several double fluorides of the type M^IF,TaF_5 have also been described.[2] Hydrogen peroxide converts the potassium salt, K_2TaF_7, into the *peroxyfluoride*, $2KF,TaO_2F_3,H_2O$, which crystallises in colourless plates (Piccini).

Tantalum Pentachloride, $TaCl_5$, is obtained by heating an intimate mixture of the pentoxide and carbon in a current of chlorine, and is also formed when the pentoxide is heated with phosphorus pentachloride. It forms light yellow needles and

[1] Melikoff and Pissarjewsky, *Zeit. anorg. Chem.*, 1899, **20**, 340.
[2] Balke, *J. Amer. Chem. Soc.*, 1905, **27**, 1140.

prisms which melt at 211° and boil at 242°, but begin to volatilise at so low a temperature as 144°, and may be readily sublimed in a current of carbon dioxide or chlorine. The specific gravity of the vapour, according to Deville and Troost, is 12·8, the calculated density being 12·42. It fumes in the air, and is converted into tantalic acid.

Tantalum Dichloride, $TaCl_2,2H_2O$, is formed when the pentachloride is heated with sodium amalgam, and separates from dilute hydrochloric acid in emerald-green, hexagonal crystals, which decompose in the air.[1]

Tantalum Pentabromide, $TaBr_5$, is prepared in a similar way to the chloride, and in its properties closely resembles this compound. Tantalum and iodine do not combine.

Tantalum and Sulphur.

440 *Tantalum Tetrasulphide*, Ta_2S_4 or TaS_2, is obtained by acting upon white-hot tantalum pentoxide, with a mixture of hydrogen and the vapour of carbon disulphide. It is a grey finely-granular friable substance which may be pressed into masses resembling graphite, and these on burnishing possess the colour of brass. It is also formed when the chloride is ignited in a stream of sulphuretted hydrogen, and is thus obtained in crusts resembling pyrites in appearance. It is not attacked by hydrochloric acid even on boiling, and nitric acid and aqua regia oxidise it but slowly.

Tantalum and Nitrogen.

441 When tantalum chloride is heated in ammonia gas to a temperature not above the point of volatilisation of the ammonium chloride which is formed, an amorphous yellowish-red mass of varying composition is obtained. If this is powdered and heated to redness in a stream of ammonia it is converted into a bright-red amorphous powder having the composition Ta_3N_5. When this is raised to a full white heat in an atmosphere of ammonia, an amorphous black powder of *tantalum nitride*, TaN, is produced which exhibits a metallic lustre on burnishing. H. Rose, who first obtained this compound, believed it to be the metal.[2] The nitride, Ta_3N_5, is also obtained

[1] Chabrié, *Compt. rend.*, 1907, **144**, 804.

[2] Muthmann, Weiss and Riedelbauch, *Annalen*, 1907, **355**, 58.

when metallic tantalum is heated in nitrogen gas to a temperature of 1000°.

Tantalum and Carbon.

Tantalum Carbide.—When 6 parts of Ta_2O_5, 1 part of sodium carbonate, and 1 part of charcoal are heated to a temperature of about 1480°, tantalum carbide, TaC, is produced in the form of fine needles.[1]

Detection and Estimation of Tantalum.

442 In order to detect tantalum in a mineral, tantalic acid must be prepared from it, and this converted into a soluble tantalate. If potassium ferrocyanide be added to this solution, a characteristic yellow precipitate falls down, and under the same circumstances tincture of galls likewise produces a bright yellow precipitate. The tantalum compounds do not colour a bead of borax or of microcosmic salt.

Tantalum is estimated quantitatively either as the pentoxide or as potassium tantalofluoride, the process having been described under columbium (p. 948).

The Atomic Weight was determined by Marignac,[2] who analysed the potassium and ammonium tantalofluorides and obtained the number 182·97. By direct conversion of the metal into the pentoxide Hinrichsen and Sahlbom[3] obtained the number 181·02. By converting the pentachloride into the oxide Balke[4] found 181·52. Chapin and Smith found 181·8 by transforming the pentabromide into the oxide.[5] The number at present (1913) adopted is 181·5.

ANTIMONY (STIBIUM). Sb = 120·2.

443 This metal occurs in nature chiefly as stibnite, antimonite, or antimony sulphide, Sb_2S_3, a mineral which was known in very early times, having been long employed, as indeed is yet the case, by women in the East for painting the eyebrows. In St. Jerome's translation of the Hebrew of Ezekiel xxiii. 40, we read "circumlinisti stibio oculos tuos"; and in the Second Book of

[1] Joly, *Compt. rend.*, 1876, **82**, 1195.
[2] *Ann. Chim. Phys.*, 1866, [4], **9**, 251.
[3] *Ber.*, 1906, **39**, 2600. [4] *J. Amer. Chem. Soc.*, 1910, **32**, 1127.
[5] *J. Amer. Chem. Soc.*, 1911, **33**, 1497.

Kings ix. 30, we find, "Porro Jezebel introitu eius audito depixit oculos suos stibio." Of this latter passage Cheyne and Driver give as the translation of the Hebrew, "set her eyes in paint (literally antimony)."

The name for this mineral in Hebrew and Arabic is "Kohl," and this word passed as "alcool" or "alkohol" into other languages; thus in the Spanish translation of the Bible the above passage from Ezekiel is thus rendered, "Alcoholaste tus ojos." In the middle ages the word alcohol served to designate any fine powder, and it was only at a later period that it was employed to mean spirits of wine. Dioscorides calls this metal *στίμμι*, and mentions that it is also known by other terms, such as *πλατυόφθαλμον*, the eye-expander, *γυναικείον*, belonging to womankind, &c. Pliny, on the other hand, terms it *stibium*. The Latin Geber, who also was acquainted with this substance, termed it *antimonium*, and up to the time of Lavoisier both these words were made use of to signify sulphide of antimony. The German name for this substance was *spiessglas*, which was afterwards changed to *spiessglanz*. As already mentioned (Vol. I., p. 9), the works attributed to "Basil Valentine," which have hitherto been regarded as the earliest known records concerning antimony and its derivatives, have been shown by the late Prof. Schorlemmer to be forgeries dating from about 1600.[1] There is no doubt, however, that the iatro-chemists, from the time of Paracelsus, were acquainted with many antimonial preparations, and numerous references to these are scattered throughout the chemical literature of those times. The statements of "Basil Valentine" may still serve to show the condition of knowledge concerning antimony in 1600. He makes the following remarks as to the name of the sulphide in his *Triumphal Car of Antimony*: "In order, as is most proper, that I may say something about the name of the material, it should be understood that this material was long known to the Arabians, and from ancient time was termed by them *asinat*. The Chaldeans entitled it *stibium*, and in the Latin tongue it has been called *antimonium*[2] up to the latest times, and in our

[1] MSS. deposited in the library of the University of Manchester. See also Pierce, *Science*, 1898, **8**, 169, who comes to the same conclusion, chiefly from a study of the contents of Basil Valentine's works.

[2] The story of the accidental poisoning of certain monks by spiessglas having given rise to the name of the metal (antimoine) is on the face of it improbable, and must, as Kopp remarks, have been invented by a Frenchman, whereas Valentine wrote in German!

own German mother tongue the same material has been foolishly called spiessglas for this reason, that this material can be fluxed and a glass made from it."

Dioscorides mentions that in order to roast the crude antimony it must be heated in a current of air until it burns, for if more strongly ignited, it melts like lead. This passage has given rise to the supposition that the author was acquainted with metallic antimony, and that this is probably the case is shown by the fact that an old Chaldean vase analysed by Berthelot consisted of pure antimony.[1] Antimony was confounded with bismuth by some chemists, such as Libavius, even so late as the sixteenth century.

The preparation of the metal was described by "Basil Valentine," who in his *Wiederholung des Grossen Steins der uralten Weisen* terms it *spiessglas rex* and also *plumbum antimonii*. It has already been stated that the alchemists considered that each semi-metal was simply a variation of a true metal.

444 Antimony occurs in many other minerals besides stibnite. The metal is found, though not frequently, in the native state, and also as arseniferous antimony or allemontite (AsSb). Antimony also occurs as the trisulphide, Sb_2S_3, combined with basic sulphides, and in these thioantimonites a portion of the antimony is usually replaced by arsenic. Amongst such compounds are berthierite, FeS,Sb_2S_3; wolfsbergite or antimonial copper, Cu_2S,Sb_2S_3; boulangerite, $5PbS,Sb_2S_3$; jamesonite $2PbS,Sb_2S_3$; bournonite, $2PbS,Cu_2S,Sb_2S_3$; pyrargyrite or red silver ore, $3Ag_2S,Sb_2S_3$, &c. In addition to these we have dyscrasite or antimonial silver, Ag_3Sb; breithauptite or antimonial nickel, NiSb, ullmannite or nickeliferous grey antimony, NiSbS; valentinite or antimony oxide, Sb_2O_3; cervantite or antimony ochre, Sb_2O_4 and stiblite, Sb_2O_4,H_2O. Antimony is also found in small quantity in iron ores, ferruginous waters, in the coal formation, and in river sand.

445 *Preparation of Metallic Antimony.*[2]—The preparation of the metal from the sulphide is a very simple operation. In order to free the ore from quartz or other earthy admixture, the mineral is either melted in vertical cylinders which have a hole at the bottom out of which the molten sulphide drops, or the

[1] *Compt. rend.*, 1887, **104**, 265.

[2] For full particulars see *Antimony*, by C. Y. Wang (C. Griffin & Co., 1909).

preliminary fusion is carried on in reverberatory furnaces. The purified sulphide is then either fused with metallic iron, or is roasted in order to convert it into oxide, which is reduced with carbon or with crude tartar. "Basil Valentine" describes both of these methods in his account of the preparation of the philosopher's stone; he states: "Antimonium is a master in medicine, and from it by means of cream of tartar and salt a King (regulus) is made, steel-iron being added to the spiessglas during fusion. Thus by an artifice a wonderful star is obtained which the learned before my time have termed the philosophical signet star." In the *Triumphal Car of Antimony* he gives the following receipt: "Take good Hungarian spiessglas and with the same quantity of crude tartar, and half as much saltpetre; rub these small and let them fuse well in a wind furnace; afterwards pour out into a mould and allow to cool when a regulus is found."

In the English process three operations are used for the production of the best star-antimony. The first of these is termed "singling"; in this 40 parts of the liquated sulphide are mixed with about 18 parts of thin scrap iron and 4 parts of salt; and this is then melted in plumbago crucibles, when metallic antimony and iron sulphide are formed. The fusion lasts about an hour and a half, and when complete the charge is poured into conical moulds. The crude metal is then separated from the slag, consisting chiefly of sulphide of iron, which floats on the surface, and it is again melted in the second process of "doubling," with an addition of a small quantity of liquated stibnite, sodium sulphate or salt, and slag obtained in the following operation. The charge for each pot is 80 lbs. of crude antimony, 7 lbs. of liquated stibnite, 2 lbs. of saltcake, and 2lbs. of slag, and the fusion lasts about an hour and a half. The metal is cast in moulds, allowed to cool, and broken into small pieces ready for the third process, termed "melting for star-metal." For this purpose 2 parts of pearl-ash and 5 parts of slag from a previous operation of the same kind are added to 60 parts of metal, and the fusion is repeated. The molten metal is then poured into square moulds in which it is allowed to cool slowly, the surface being at the same time completely covered with slag in order that it may attain the peculiar crystalline structure which is required in commerce.

In the roast and reduction method for the extraction of antimony, two distinct processes are in use; in the first, the

sulphide ore is roasted to the stable tetroxide, generally in reverberatory or muffle furnaces at a temperature of about 350°. In the second process the volatile trioxide is formed by restricting the amount of air admitted, and working at a higher temperature. The volatile trioxide is condensed in suitable pipes and chambers. This latter process has several advantages, for low grade ores may be treated with success, arsenic may be separated owing to the more volatile nature of arsenic oxide, and in the case of ores containing precious metals, these may be extracted from the residues.

The oxide of antimony obtained by either process may be reduced to the metallic state by fusion with coal or charcoal, together with alkaline fluxes such as potash, soda, etc., in small reverberatory furnaces or crucibles.

It has been stated already that "Basil Valentine" was acquainted with the crystalline surface exhibited by pure antimony, but he specially mentions that the regulus which is not starred possesses exactly the same composition as that which presents this peculiarity. He, as well as some of his contemporaries, believed that the stellated surface was produced only when iron was employed in the preparation, whilst other chemists taught that the preparation of the stellated antimony did not depend on the presence of iron, but was connected with a favourable conjunction of the stars. Indeed this latter opinion was pretty generally held until the time of Boyle, who however entirely discredits this explanation, and also states that the starred metal can be obtained without the use of iron.

In his essay *On the Unsuccessfulness of Experiments*, Boyle[1] says: "And it may perhaps also be from some diversity either in antimonies or irons, that eminent chemists have (as we have observed) often failed in their endeavours to make the starry regulus of *Mars* and antimony. Insomuch that divers artists fondly believe and teach (what our experience will not permit us to allow) that there is a certain respect to times and constellations requisite to the producing of this (I confess admirable) body. Upon this subject I must not omit to tell you that a while since an industrious acquaintance of ours was working on an antimony, which unawares to him, was, as we then supposed, of so peculiar a nature, that making a regulus of it alone without iron, the common way (for his manner of operation I inquired of him), he found, to his wonder, and showed me his regulus

[1] *Opera*, ed. 1772, **1**, 325.

adorned with a more conspicuous star than I have seen in several stellate reguluses of both antimony and *Mars.*"

Lemery, in his *Cours de Chymie*, published in 1675, also argues strongly against the supposition that the planet Mars has anything to do with the formation of the stellated surface.

Commercial antimony often contains traces of silver, gold, arsenic, iron, lead, copper, and frequently some sulphur. In order to prepare the pure metal Liebig's process may be used; this consists in fusing 16 parts of the metal with two parts of sodium carbonate, and 1 part of sulphide of antimony for an hour; on cooling, the regulus is separated from the slag, and melted again for an hour with $1\frac{1}{2}$ parts of sodium carbonate, and this operation again performed with 1 part of this salt.[1] According to Schiel[2] a small quantity of nitre should be added from time to time. By means of this repeated fusion the whole of the arsenic is separated, provided that a sufficient quantity of iron be originally present in the metal; should this not be the case, it is necessary to add about 2 per cent. of iron sulphide.[3]

Another method of purifying the metal is that described by Wöhler, and improved by Meyer,[4] and this is available when the only impurity present is arsenic. In this process, one part of the metal is ignited with 1·25 parts of sodium nitrate, and 0·5 part of sodium carbonate. The pulverised mass is dissolved in water when pure sodium metantimonate remains behind; this is then reduced by heating with half its weight of cream of tartar or with a mixture of carbon and sodium carbonate.

446 *Properties.*—Antimony is a lustrous silver-white metal, which when slowly cooled exhibits a coarsely laminated crystalline fracture. When quickly cooled, on the other hand, the fracture is granular. It crystallises in obtuse rhombohedra which can scarcely be distinguished from cubes, and has a specific gravity of 6·71 to 6·86. Native antimony occurs in scaly masses, usually containing silver, iron, and arsenic. Its most important localities are at Sahl in Sweden, Andreasberg in the Harz, Przibram in Bohemia, in the Dauphiny, in Canada, the United States, Mexico, Chili, Sarawak, in Borneo and Queensland. Native antimony has a specific gravity of from 6·5 to 7.

Antimony is hard, and so brittle that it can be powdered; it

[1] *Annalen*, 1857, **104**, 223.
[2] *Annalen*, 1835, **19**, 22.
[3] Bensch, *Annalen*, 1847, **63**, 273.
[4] *Annalen*, 1848, **66**, 238.

melts at 630·5°,[1] and volatilises at a bright red heat in the air, or in a current of a gas, but not when fused under a layer of common salt. It may be distilled in a current of hydrogen at a white heat. The vapour density of antimony is 10·743 at 1572°, and 9·781 at 1640° (Meyer and Biltz),[2] numbers which are intermediate between those required for the molecular formulæ Sb_2 and Sb. It does not undergo any alteration on exposure to the air at the ordinary temperature; on heating it burns to form the oxide, and when heated on charcoal before the blowpipe, the oxide is evolved in thick white fumes, and a portion of it is deposited as a white incrustation on the charcoal. If the blast of air be stopped the globule of molten metal begins to glow, and is seen to be covered with a crystalline network of needles of oxide, and when the globule is thrown from some height on to a piece of paper, the edges of which are turned up, it breaks into many smaller globules which burn with a very bright flame. Neither cold water nor dilute sulphuric acid acts upon the metal at the ordinary temperature, but at a red heat it decomposes steam with formation of oxide. Nitric acid converts it into a white powder, the composition of which depends on the strength of the acid, nitrogen peroxide being evolved and no ammonia formed.[3] Pure antimony does not dissolve in strong hydrochloric acid in the absence of oxygen,[4] but the ordinary metal is easily dissolved by hot hydrochloric acid as well as by cold aqua regia, and when heated with concentrated sulphuric acid is converted into antimony sulphate. Antimony combines directly with the elements of the chlorine group, with those of the sulphur group, and with phosphorus and arsenic.

Allotropic Modifications of Antimony.—The grey, metallic form of antimony described above is the stable modification, but unstable yellow and black modifications, corresponding with the unstable yellow and stable grey forms of arsenic (Vol. I., p. 684) also exist.[5] The yellow form is obtained by the action of oxygen on liquid stibine at –90°, and by the action of chlorine on stibine, both dissolved in liquid ethane at – 100°. It is amorphous, appears to dissolve slightly in carbon

[1] Holborn and Day, *Ann. Physik*, 1900, [4], **2**, 505. See also Heycock and Neville, *Journ. Chem. Soc.*, 1895, **67**, 186.

[2] *Ber.*, 1889, **22**, 725. See also *Annalen*, 1887, **240**, 317.

[3] Montemartini, *Gazz.*, 1892, **22**, 384.

[4] Ditte and Motzner, *Compt. rend.*, 1892, **115**, 936.

[5] Stock and Guttmann, *Ber.*, 1904, **37**, 885; Stock and Siebert, *Ber.*, 1905, **38**, 3837.

disulphide, and passes very readily, when the temperature rises above −90°, into the black variety. The latter can also be prepared by the rapid cooling of antimony vapour, and by the action of oxygen on liquid stibine at −40°. It is an amorphous black powder, has the specific gravity 5·3, oxidises spontaneously in the air, sometimes taking fire, and passes when heated into the stable metallic form with evolution of heat.

Explosive or Electrolytic Antimony.—This peculiar substance, discovered by Gore,[1] is obtained by electrolysis of an acid solution of antimony trichloride having a specific gravity of 1·35, or of a solution obtained by dissolving the trioxide in from 5 to 6 times its weight of hydrochloric acid of specific gravity 1·12, metallic antimony being, in each case, used as the positive, and copper or platinum as the negative pole. The latter becomes covered with a grey lustrous metallic coating, having an amorphous fracture and a specific gravity of 5·78. It contains from 4·8 to 7·9 per cent. of antimony chloride, together with a small quantity of free hydrochloric acid. When scratched with a metallic point or touched with a red-hot wire it decomposes with evolution of heat and liberation of the chloride, and when heated to 200° it flies into powder with a loud explosion. If it be preserved under cold water it does not immediately undergo any alteration, but when heated to 75° it decomposes with a hissing sound; hydrochloric acid is found in solution, and the water becomes turbid owing to the formation of basic antimony chloride. Similar products are obtained by the electrolysis of acid solutions of the bromide and iodide (Gore), but not of the fluoride.

This remarkable substance is probably a solid solution of an antimony halogen compound in an allotropic form of antimony, and the explosion consists in the sudden transformation of the latter into the stable metallic form, the heat evolved amounting to 20 cal. per gram; the same change goes on slowly when the explosive material is preserved.[2] This form is possibly identical with the black amorphous form described above, but the identity has not been definitely proved.

Uses.—Antimony is employed for the preparation of tartar emetic, and of other products used in pharmacy and in many

[1] *Phil. Trans.*, 1858, **148**, 185; 1859, **149**, 797; 1862, **152**, 323; Pfeifer, *Annalen*, 1881, **209**, 61.

[2] Cohen and Ringer, *Zeit. physikal. Chem.*, 1904, **47**, 1; Cohen, Collins and Strengers, *ibid.*, 1905, **50**, 291; Cohen and Strengers, *ibid.*, 1905, **52**, 129.

processes of calico printing and dyeing. Its alloys are also largely used in the arts. When antimony is precipitated by zinc from a solution of the trichloride, the metal is obtained in a finely pulverulent state, as *antimony black*; this is employed for the purpose of imparting to the surface of gypsum figures and other objects the appearance of iron or steel.

Antimony Alloys.

447 "Basil Valentine" mentions that antimony is valuable for the preparation of medicines, and that it is likewise employed for other purposes, such as for the preparation of printers' type. He adds that under certain favourable conjunctions of the planets alloys are made of antimony, and from these seals and amulets are cast, which are said to possess special virtues. These same alloys can, according to Valentine, be cast in the same way to form both bells and mirrors.

English type metal is an alloy of lead, antimony, and tin. A small percentage of copper is sometimes added, but is found of little practical value. The value of antimony in these alloys is that it imparts to them hardness, and gives them the property of expanding in the act of solidification so necessary in order to obtain an accurate cast of the letter. The tin gives toughness and coherence to the metal. The following are analyses of English type metal:

	I.	II.	III.	IV.	V.	VI.	VII.
Lead	50	60·0	61·3	69·2	85·7	83·5	80·0
Antimony . .	25	30·0	18·8	19·5	14·3	13·5	15·0
Tin	25	10·0	20·2	9·1	—	3·0	5·0
Copper . . .	—	—	—	1·7	—	—	—

No. I is supposed to give the best results for high class work, but owing to the high price of tin No. II. is generally used. No. V is used for stereotype plate, No. VI is linotype metal, and No. VII. monotype metal.

Britannia metal and *Pewter*.—This silver-white metal is largely used for the preparation of spoons, cups, and other articles. It consists mainly of tin and antimony, but frequently contains other metals, as is shown by the following analyses:

	Britannia Metal.		Plate. Pewter.	Ashbury Metal.	Metal Argentum.
Tin	85·7	81·9	89·3	77·8	85·5
Antimony . . .	10·4	16·2	7·1	19·4	14·5
Copper	1·0	—	1·8	—	—
Zinc	2·9	1·9	—	2·8	—
Bismuth . . .	—	—	1·8	—	—

White or *anti-friction metal* is chiefly used for lining the brasses of various parts of locomotive engines, and for the solid pushes for the coupling-rods. Several alloys are used for this purpose, as is seen by the following analyses:

	I.	II.	III.
Copper	5·3	1·5	—
Antimony	10·5	13·0	20
Tin	84·2	45·5	20
Lead	—	44·0	60

The alloy employed for the manufacture of ships' nails consists of 3 parts of tin, 2 of lead, and 1 of antimony.

Brass articles can be covered with a fine lustrous coating of antimony by dipping them into a hot solution of 1 part of tartar emetic, 1 of tartaric acid, and 3 of water, to which 3 or 4 parts of hydrochloric acid and as much powdered antimony have been added.

Antimony forms a beautiful purple alloy with copper which has the composition Cu_2Sb, and is known as Regulus of Venus

COMPOUNDS OF ANTIMONY.

Antimony and Hydrogen.

448 *Antimony Hydride* or *Stibine*, SbH_3.—This substance was first prepared in 1837 by Lewis Thompson,[1] and also independently by Pfaff[2] and other chemists. It is formed when nascent hydrogen is brought into contact with a soluble antimony compound, or when an alloy of potassium or sodium with antimony is decomposed by water, or an alloy of zinc and

[1] *Phil. Mag.*, 1837, [3], **10**, 353. [2] *Pogg. Ann.*, 1837, **42**, 339.

antimony by dilute hydrochloric or sulphuric acid. It is also formed when antimony oxide is added to an acid solution which is evolving hydrogen. All these methods, however, furnish a gas which is largely mixed with free hydrogen,[1] and the preparation of pure stibine is a matter of some difficulty. The liquefied gas was first obtained by Olszewski [2] in 1886, and the pure gas itself by Stock and Doht [3] in 1901. A gas containing as much as 14 per cent. of stibine is first prepared by gradually bringing a powdered alloy of 1 part of antimony and 2 parts of magnesium, prepared by heating the constituents to redness in an atmosphere of hydrogen, into hydrochloric acid of sp. gr. 1·06 at 0°, which has been previously boiled. When this gas is washed through water, dried over calcium chloride and phosphoric oxide, and cooled by liquid air, it yields a white mass of solid stibine, and this on evaporation gives pure stibine, free from admixed hydrogen. The gas thus prepared can be collected over mercury, and when dry can be preserved for some hours without undergoing decomposition. It is a colourless gas with a characteristic odour, faintly resembling that of sulphuretted hydrogen, and is very poisonous. It condenses to a colourless liquid, which boils at −17°, and solidifies to a white mass, melting at −88°. The density of the gas is 4·36 at 15° and 760 mm., this being about 2·95 per cent. greater than the calculated normal density. The density of the liquid is 2·26 at −25°. Water dissolves about 0·2 vol. of the gas, and in the absence of impurities the solution is stable for some time, whilst in the presence of mere traces of air decomposition sets in rapidly. Alcohol dissolves 15 vols. of the gas, and carbon disulphide 250 vols., but both of these solutions are very unstable. Stibine decomposes slowly at the ordinary temperature into antimony and hydrogen, one volume yielding 1·544 vols. of hydrogen. The rate of decomposition has been carefully studied,[4] and is greatly accelerated by the presence of water, of metallic antimony, or of hydrogen chloride. The gas is formed from its elements with absorption of 84,500 cal.,[5] and

[1] See Jones, *Journ. Chem. Soc.*, 1876, i., 641.

[2] *Monatsh.*, 1886, **7**, 371 ; *Ber.*, 1901, **34**, 3592.

[3] *Ber.*, 1901, **34**, 2339 ; 1902, **35**, 2270 ; Stock and Guttmann, *Ber.*, 1904, **37**, 885.

[4] Stock and Guttmann, *Ber.*, 1904, **37**, 901, 1957 ; Bodenstein, *Ber.*, 1904, **37**, 1361 ; Stock, Gomolka and Heynemann, *Ber.*, 1907, **40**, 532 ; Stock, Echeandia and Voigt, *Ber.*, 1908, **41**, 1309.

[5] Berthelot and Petit, *Compt. rend.*, 1889, **108**, 546.

explodes when a spark is passed through it, or when it is strongly heated. Spontaneous explosion also occurs occasionally and may extend to the liquid.

Stibine is very readily decomposed by oxygen and air, with formation of water and metallic antimony, and is also attacked by nitric and nitrous oxides, and explodes when brought into contact with chlorine.

Stibine is easily inflammable, burning with a greyish flame, and evolving white fumes of antimony oxide. When the gas is passed through a glass tube heated above 150° metallic antimony is deposited close to the heated spot in the form of a lustrous mirror, and if this be heated more strongly, small metallic globules are seen by the microscope to have been formed. Concentrated sulphuric acid decomposes the gas. Caustic alkali solution becomes deep brown when the gas is passed through it, and at last a black powder separates out. The brown solution absorbs oxygen rapidly, and especially if it be shaken with air. The powder thus obtained appears to possess the composition $Sb(OH)_3$. It rapidly decomposes on standing, becoming richer in antimony. When antimony hydride is passed through a solution of silver nitrate, black silver antimonide, $SbAg_3$,[1] is first formed; the excess of silver nitrate present, however, causes a further reaction to take place, and the final precipitate obtained consists of silver and antimony hydroxide, with a little metallic antimony.[2] Sulphur decomposes the gas and becomes itself covered with a film of the orange-red antimony sulphide (Jones):

$$2SbH_3+6S=Sb_2S_3+3H_2S.$$

Sulphuretted hydrogen has no action on the pure gas, but readily decomposes the impure mixture with hydrogen.

Antimony and Oxygen.

449 Considerable doubt formerly existed as to the number of the oxides formed by antimony. Thénard, in 1800, mentions several; whilst Proust, in 1804, admitted the existence of only two. The exact number was ascertained by Berzelius in 1812 to be as follows:

Antimony trioxide, Sb_4O_6,
Antimony tetroxide, Sb_2O_4,
Antimony pentoxide, Sb_2O_5.

[1] Lassaigne, *J. Chim. Méd.*, 1840, **17**, 443.

[2] Reckleben, *Ber.*, 1909, **42**, 1458; see also Vitali, *L'Orosi*, 1892, 397.

All these are acid-forming oxides; the first acting also as a feebly basic oxide.

Antimony Trioxide, Sb_4O_6.—This occurs as the mineral valentinite with other ores of antimony, having been produced by the oxidation of these. It forms pearly-white rhombic crystals which are sometimes coloured yellow or red by the presence of iron and other metals, and have a specific gravity of 5·566. Another, though less frequent form of antimony trioxide, is senarmontite, which usually occurs together with other antimony ores, and crystallises in regular octahedra, having a specific gravity of 5·2 to 5·3. From this it appears that antimony trioxide is isodimorphous with arsenious oxide (p. 219). Both these crystalline forms can be artificially prepared. Thus when the metal or sulphide is heated in an inclined crucible a light white oxide is formed at a red heat, and this when more strongly heated is deposited on the upper part of the crucible in glistening needles, sometimes mixed with octahedra, and known as *flores antimonii*, or flowers of antimony. This latter form is also observed when the rhombic oxide is sublimed, and the octahedra, when quickly heated, are converted into the rhombic crystals.[1] Both forms are also obtained by crystallising a hot saturated solution of the oxide or chloride in sodium carbonate (Mitscherlich). Antimony trioxide is prepared by diluting an acid solution of the oxide with water, and washing the basic salts which are thrown down, first with hot water, then with sodium carbonate solution, again with water, and finally converting the residue into oxide by ignition. Obtained in this way, the oxide is a pale buff-coloured crystalline powder, which can also be obtained, but not perfectly pure, by oxidising the metal with very dilute nitric acid. It is scarcely soluble in water, and becomes yellow when ignited, but assumes the pale buff tint again on cooling.

At a dark red heat it melts, and the mass obtained on cooling is crystalline. It volatilises at 1560°, yielding a vapour having a specific gravity of 19·9, corresponding to the molecular formula Sb_4O_6.[2] It is insoluble in dilute sulphuric acid and in nitric acid, but is easily soluble in hydrochloric and tartaric acids, and the caustic alkalis. The solution of antimony trioxide in cream of tartar yields *potassium antimonyl tartrate* or *tartar emetic*, $C_4H_4KSbO_7$. Heated in the air it absorbs oxygen, the

[1] Terreil, *Compt. rend.*, 1866, **62**, 302.
[2] V. and C. Meyer, *Ber.*, 1879, **12**, 1282.

tetroxide[1] being formed at all temperatures between 390–775°; at very high temperatures, however, the latter decomposes and the trioxide is again formed.[2] The trioxide is readily reduced when it is heated in hydrogen. According to Bunsen, the presence of higher oxides can be easily detected by the addition of potassium iodide to the hydrochloric acid solution, when iodine is set free, as may be readily ascertained by shaking the liquid with a few drops of carbon disulphide.

The trioxide in solution is readily converted into antimonic acid by means of oxidising agents such as iodine, chlorine, or potassium dichromate, but the change cannot be completely effected by bromine water, nitric acid, or potassium chlorate and hydrochloric acid.[3] It reduces the salts of many of the metals.[4]

The mineral valentinite was probably known to the ancients. Pliny states that two kinds of stibium exist: "*Duo ejus genera mas et femina. Horridior est mas scabriorque et minus ponderosus, minusque radians et arsenosior; femina contra nitet, friabilis, fissurisque, non globis, dehiscens.*" Perhaps, however, under the feminine variety he may have understood the preparation obtained by roasting the sulphide, for this process is mentioned by Dioscorides, and Glauber also refers to it. The operation is more fully described by "Basil Valentine." He says that by regulating the fire carefully "from the common regulus of the spiessglas magnificently fine *flores* may be prepared, both yellow, red, and white." Valentine certainly knew that the mineral which we now call valentinite is an ore of antimony, for he distinguishes between the black and the golden spiessglas. The oxide obtained by roasting the metal reduced by iron was formerly called *nixferrum*, as it was believed that iron was necessary for its formation.

Antimony trioxide acts as a weak acid-forming oxide and also as a weak basic oxide. The salts formed by the action of strong acids are decomposed by water with formation of basic salts, which in contact with water are gradually converted into the oxide.

Antimonious Acid.—Two hydrates of antimony trioxide have been described, which may be considered as the ortho- and

[1] Carnelley and Walker, *Journ. Chem. Soc.*, 1887, **53**, 86.

[2] Read, *Journ. Chem. Soc.*, 1894, **65**, 314; Baubigny, *Compt. rend.*, 1897, **124**, 499, 560.

[3] Bošek, *Journ. Chem. Soc.*, 1895, **67**, 515.

[4] Harding, *Zeit. anorg Chem.*, 1899, **20**, 235.

pyro-acids, although it is not certain that they are definite compounds, since the amount of water contained in them varies gradually with the temperature at which they are dried. The ortho-acid, H_3SbO_3, is obtained by adding nitric acid to antimonyl tartaric acid or tartar emetic, and drying the precipitate at 100°. The pyro-acid, $H_4Sb_2O_5$, is formed by adding copper sulphate to a solution of antimony sulphide in caustic potash until no further orange-coloured precipitate is thrown down, but a white precipitate is formed. After filtration the liquid, on addition of acetic acid, yields a precipitate having the above composition.[1]

Only sodium and potassium salts have as yet been obtained in the crystalline condition, and these appear to be salts of the (unknown) meta-acid, $HSbO_2$.

Sodium Antimonite, $NaSbO_2,3H_2O$, separates out from a hot solution of the oxide in caustic soda in glistening octahedra, which are sparingly soluble in water.

Hydrogen Sodium Antimonite, $NaSbO_2,2HSbO_2$, is obtained from very concentrated solutions in large crystals almost insoluble in water, which, like those of the former compound, appear to belong to the monoclinic system.[2]

Potassium Triantimonite, $K_2O,3Sb_2O_3$, is formed in crystals when the trioxide is boiled with caustic potash.[3]

Antimony Tetroxide or *Antimonious-Antimonic Oxide*, Sb_2O_4.—This oxide is a white powder formed when either of the two other oxides is strongly heated in the air. When heated it becomes temporarily yellow, and dissolves only with difficulty in acids. Antimony-ash, obtained by roasting the sulphide in the air, is an impure tetroxide, and was formerly employed for the preparation of the antimony compounds. Impure tetroxide also occurs as the mineral cervantite, found together with other antimony ores in Tuscany. Antimony tetroxide forms salts with basic oxides which have been termed *hypoantimonates*.

Potassium Hypoantimonate, $K_2Sb_2O_5$, is obtained by fusing together the tetroxide and potash, and lixiviating with cold water. It is a white mass which is soluble in hot water; on addition of hydrochloric acid to this solution the salt $K_2Sb_4O_9$ separates out.

Other insoluble hypoantimonates can be obtained by double

[1] Schaffner, *Annalen*, 1844, **51**, 182.
[2] Terreil, *Ann. Chim. Phys.*, 1866, [4], **7**, 380.
[3] Cormimbœuf, *Compt. rend.*, 1892, **115**, 1305.

decomposition with the corresponding salts. Some of these occur as minerals. Thus romeite, $CaSb_2O_5$, crystallises in tetragonal pyramids, and is found at St. Marcel, in Piedmont; and ammiolite which occurs as a powder coloured red by the presence of cinnabar, found in Chili, is probably a copper hypoantimonate, $CuSb_2O_5$.

Antimony Pentoxide and the Antimonic Acids.

450 *Antimony Pentoxide*, Sb_2O_5, is obtained by rapidly evaporating the powdered metal or its lower oxides with nitric acid, and gently heating the residue. This product usually contains a small amount of the lower oxides, but the pure oxide may be prepared by gently heating the precipitate produced by adding dilute nitric acid to a solution of potassium antimonate. It is a light yellow powder, having a specific gravity of 5·6, practically insoluble in water, and turning blue litmus paper red. Nitric acid does not dissolve it, whilst concentrated hydrochloric acid attacks it only slowly, but at last dissolves it completely; it volatilises completely when heated with sal-ammoniac. It is reduced to the trioxide when it is heated with hydriodic acid, or treated with stannous chloride solution. Antimony pentoxide acts as a stronger acid-forming oxide than the trioxide, and at the same time as a weaker base, the only stable salts being the sulphide, fluoride, and chloride, all of which have the typical formula SbR^{I}_{5}.

Antimonic Acid.—Antimony pentoxide is said to form several distinct hydrates, which correspond in composition to the hydrates of phosphorus pentoxide, and are known by similar names. A certain amount of confusion exists in the nomenclature of these acids since Berzelius gave the name of antimonic acid to the hydrate, $HSbO_3$, the true metantimonic acid, whereas the true pyroantimonic acid, $H_4Sb_2O_7$, was termed metantimonic acid by Frémy, and the same system extended to the salts.

The hydrated pentoxide which is formed by the action of cold water on the pentachloride, or by oxidising antimony trichloride with nitric acid, and precipitating by water, is moderately soluble in water. According to Delacroix,[1] this solution contains pyroantimonic or tetra-antimonic acid, which is converted by boiling into the ortho- or tri-antimonic acid, and

[1] *J. Pharm.*, 1897, [6], **6**, 337; *Bull. Soc. chim.*, 1899, [3], **21**, 1049; 1900, [3], **25**, 288.

yields salts of the types $M_2O,4Sb_2O_5$ and $M_2O,2Sb_2O_5$, whereas Senderens[1] describes the preparation of metantimonates from the same solution.

The composition of all the acids which have been prepared in the solid state depends on the temperature at which they have been dried, and it is very doubtful whether they are really definite hydrates.

The *ortho-acid*, H_3SbO_4, is formed when potassium antimonate is decomposed by dilute nitric acid and the precipitate dried at 100°. The *meta-acid*, $HSbO_3$, is formed when this is heated to 175°. These substances are white powders which are soluble in aqueous potash, slightly soluble in water, and are converted into the pentoxide when heated. The meta-acid was formerly known under the name of *materia perlata*, and was employed as a medicine.

The *pyro-acid*, $H_4Sb_2O_7$ (Frémy's metantimonic acid), is formed by the decomposition of the pentachloride by hot water. The air-dried precipitate[2] possesses the formula $H_4Sb_2O_7,2H_2O$, and has the same composition as volgerite, a mineral which occurs in the province of Constantine, in Algeria. When dried at 100° it becomes anhydrous, and it dissolves rather more readily in water than antimonic acid, and is soluble also in cold ammonia. When heated to 200°, or when kept under water, it is converted into metantimonic acid.

The Antimonates.—Since the time of Berzelius, the antimonates have been chiefly investigated by Frémy,[3] Heffter,[4] Beilstein and Bläse,[5] Knorre and Olschewsky,[6] Ebel,[7] Delacroix, and Senderens.

Considerable doubt still exists as to the constitution of these compounds, since most of them contain water, and it is uncertain whether this belongs to the constitution of the salt or is water of crystallisation.

Potassium Antimonate, $KSbO_3$, is obtained by deflagrating one part of metallic antimony with four parts of saltpetre and lixiviating with warm water. A white powder is thus obtained, which when boiled for some time with water dissolves to a considerable extent. On concentrating the solution to a certain

[1] *Bull. Soc. chim.*, 1899, [3], **21**, 47.
[2] Daubrawa, *Annalen*, 1877, **186**, 110.
[3] *Ann. Chim. Phys.*, 1844, [3], **12**, 499; 1848, [3], **23**, 407.
[4] *Pogg. Ann.*, 1852, **86**, 418.
[5] *Journ. Chem. Soc.*, 1889, **56**, 1123.
[6] *Ber.*, 1887, **20**, 3043.
[7] *Ber.*, 1889, **22**, 3044.

point, a crystalline mass separates, but if the liquid be further evaporated, a gum-like mass, $2KSbO_3,nH_2O$, is obtained which dissolves readily in warm water. When dried at 100° this salt contains $3H_2O$, and at 185° still contains $2H_2O$. When a current of carbon dioxide is passed through a solution of the normal salt, a sparingly soluble acid salt is precipitated which has the formula $2K_2O,3Sb_2O_5,7H_2O$ at 100°, and still contains $2H_2O$ at 350°. This salt was probably known to the iatro-chemists, and was much employed by quack doctors and known as *antimonium diaphoreticum ablutum*. The substance obtained by deflagrating the sulphide with saltpetre was employed at the end of the seventeenth century under the name *antimonium diaphoreticum non ablutum*, and Libavius and others treated this residue with acids in order to obtain their diaphoreticum, which, therefore, consisted chiefly of antimonic acid.

Normal Potassium Pyroantimonate, $K_4Sb_2O_7$, was described by Frémy (under the name of metantimonate), but the substance obtained by him was probably a mixture of caustic potash and potassium antimonate. A sparingly soluble *acid salt*, $K_2H_2Sb_2O_7,7H_2O$, can, however, be prepared by oxidising an alkaline solution of potassium antimonite with potassium permanganate and evaporating the filtrate (Knorre and Olschewsky).[1]

Sodium Antimonate, $2NaSbO_3,7H_2O$, is obtained when the metal or sulphide is deflagrated with Chili saltpetre and the mass washed out with water. At 200° it loses two molecules of water, but it does not become anhydrous until it attains a red heat.

A salt which is probably identical with this is formed as a voluminous white precipitate when sodium chloride is added to a solution of the gummy potassium antimonate. This changes on standing into the crystalline *acid sodium pyroantimonate*, $H_2Na_2Sb_2O_7,6H_2O$. This salt is only soluble in 350 parts of cold water, and is the least soluble of the inorganic salts of sodium. A solution of potassium antimonate can therefore be used as a reagent for the detection of sodium. Even when a solution contains only 0·1 per cent. of sodium salt a crystalline powder separates out after standing for twelve hours. Addition of alcohol facilitates the precipitation; free alkalis, on the other hand, retard its formation. The salts of lithium, ammonium, and the metals of the alkaline earths give precipitates with potassium metanti-

[1] *Ber.*, 1885, **18**, 2353.

monate, and hence these substances must be removed from solution before the above test for sodium can be applied.

Ammonium Antimonate, NH_4SbO_3, is formed by dissolving the acid in warm ammonia. It separates out on cooling as a crystalline powder, which is insoluble in water, and readily gives off ammonia. This is the only ammonium antimonate which is known.[1]

Many other salts have been prepared by the action of alkalis and metallic acetates on a solution of hydrated antimonic oxide in water (Delacroix, Senderens).

The antimonates of metals of the other groups are either sparingly soluble or insoluble in water. They may be obtained by double decomposition as crystalline precipitates, which are decomposed by weak acids with formation of acid salts, whilst stronger acids, on the other hand, liberate antimonic acid. Almost all the antimonates dissolve in strong hydrochloric acid.

Normal Lead Antimonate, $Pb(SbO_3)_2$, is a white curdy precipitate, insoluble in water. The *basic salt*, $Pb_3(SbO_3)_2(OH)_4,2H_2O$, occurs as bleinierite, at Nertschinsk, in Siberia, and Endellion, in Cornwall, in reniform or spheroidal masses, which possess a resinous appearance and a white, grey, brown, or yellowish colour. Another basic salt which is used in oil painting under the name of Naples yellow, is obtained by heating a mixture of one part of tartar emetic, two parts of lead nitrate, and four parts of common salt for two hours to the fusing point of sodium chloride, and then lixiviating with water.

Antimony and the Halogens.

451 *Antimony Trifluoride*, SbF_3, is obtained as a dense snow-white mass by distilling antimony with mercury fluoride. If a solution of the oxide in an excess of hydrofluoric acid be evaporated, the fluoride is also obtained in rhombic pyramids. It is deliquescent, and is not decomposed by water; but if the solution be evaporated without an excess of hydrofluoric acid a basic fluoride is formed. Antimony trifluoride forms crystalline double salts with the fluorides of the alkali metals, containing one molecule of the trifluoride to one, two, or three molecules of the alkali fluoride. The potassium salt is used in calico printing.

Antimony Pentafluoride, SbF_5, is obtained by boiling antimony

[1] Raschig, *Ber.*, 1885, **18**, 2743.

pentachloride with anhydrous hydrofluoric acid in a platinum retort provided with a reflux condenser of platinum for three days and fractionally distilling the residue:[1]

$$SbCl_5 + 5HF = SbF_5 + 5HCl.$$

It is a thick, colourless liquid, which has the specific gravity 2·993 at 22·7°, boils at 150°, and solidifies when cooled. It attacks the skin, and dissolves paraffin, but has no action on dry glass. Exposed to air it unites with water, forming a hydrate with $2H_2O$. It combines with antimony trifluoride, with evolution of heat and contraction, forming a series of additive compounds, varying in composition from $SbF_5,2SbF_3$ to $SbF_5,5SbF_3$. The pentafluoride forms difficultly crystallisable double salts with the fluorides of the alkali metals.[2] Chlorine has no action on the pentafluoride, but bromine forms a viscid, dark brown mass, probably containing SbF_5Br. Iodine also reacts on the pentafluoride with development of heat and the formation of a bluish-green liquid or of a dark brown solid.

When a current of ammonia is passed over the pentafluoride a vigorous action takes place and it becomes coated with a yellowish-red crust which prevents further action. When heated with liquid ammonia at 100°, a white powder is formed which is readily decomposed by atmospheric moisture.

Various compounds of antimony pentafluoride and antimony pentachloride have been described by Ruff.[3]

Antimony Trichloride, $SbCl_3$.—"Basil Valentine" says, "Take of fine white, well-sublimed corrosive sublimate, and of good spiessglas the same quantity. Rub these up together and distil them. The oil which comes over is at first white, and congeals like ice or clots of butter." This preparation was termed *butyrum antimonii*, and was supposed to contain quicksilver until Glauber, in 1648, showed that this was not the case, inasmuch as it could be prepared by distilling spiessglas with oil of vitriol and common salt or hydrochloric acid. Several other methods of preparation may be mentioned, as for example, by heating sulphate of antimony with sodium chloride, as well as by heating an excess of metallic antimony, or its sulphide, in a current of dry chlorine.

Antimony trichloride is a crystalline mass, melting at 73·2°

[1] Ruff and Plato, *Ber.*, 1904, **37**, 673; see also *Ber.*, 1906, **39**, 4310.
[2] Marignac, *Annalen*, 1868, **145**, 239. [3] *Ber.*, 1909, **42**, 4021.

and boiling at 223·5° (Kopp).[1] Its colourless vapour has the normal specific gravity of 7·8 and the salt dissolved in ether has the normal molecular weight.[2] Its latent heat of fusion is 13·37 cal. On exposure to moist air the solid deliquesces to a clear liquid, and this, on evaporation over sulphuric acid, yields crystals of the anhydrous chloride. A solution of the chloride is best obtained by boiling the sulphide with strong hydrochloric acid. When this is distilled in a retort, water comes over first, next the excess of hydrochloric acid, and lastly the anhydrous chloride. The concentrated solution, which has a specific gravity of 1·35, is known as *liquid butter of antimony*, and is employed for giving a brown surface to iron and steel wares, such, for instance, as gun-barrels (brown Bess); it is also sometimes used for pharmaceutical purposes. The anhydrous chloride yields with dry ammonia the brittle white compound $SbCl_3,NH_3$, which, on heating, gives off ammonia. It combines with hydrochloric acid to form the crystalline compound $2SbCl_3,HCl,2H_2O$ and also forms soluble crystalline double salts with a variety of metallic chlorides.[3]

Powder of Algaroth.—If the acid solution of the chloride be diluted with water a white precipitate of the basic chloride is thrown down. This precipitate was known to Paracelsus, who employed it as a medicine, and states in his *Archidoxa* that in order to prepare it, corrosive sublimate is to be distilled with antimony, and the product coagulated with water, when the *mercurius vitæ* is obtained. Towards the end of the sixteenth century it was much employed, especially by the Veronese physician, Algarotus, and was termed by him *pulvis angelicus* although it has been generally known as *powder of Algaroth*. The presence of tartaric or free hydrochloric acid prevents the precipitation of this substance. Its composition varies according to the method of its preparation. If ten parts of solid trichloride are mixed with seventeen parts of water, and allowed to stand until the precipitate has become crystalline, the compound SbOCl is deposited in small rhombohedra. These may be washed with ether in order to remove the excess of the chloride. The same compound is obtained by heating equal molecules of the trichloride and absolute alcohol in sealed tubes to 140°. If one part of the trichloride be mixed with three parts

[1] See also Beckmann, *Zeit. anorg. Chem.*, 1906, **51**, 96.
[2] Lespieau, *Compt. rend.*, 1897, **125**, 1094.
[3] See Ephraim, *Ber.*, 1903, **36**, 1815.

of water, and the precipitate filtered off quickly and mixed with ether, the same body is obtained in the form of an amorphous powder. When this substance is heated the trichloride is given off, and the oxychloride, $Sb_4O_5Cl_2$, remains behind. The last named compound is formed as an amorphous precipitate when the chloride is mixed with from five to fifty parts of water; on standing, it gradually becomes crystalline, forming silky prisms. If three times its bulk of hot water be added to the trichloride, and the liquid allowed to stand at 60° for some hours, crystals are obtained resembling soda crystals, which also possess the composition $Sb_4O_5Cl_2$.[1] When larger quantities of water are employed still more basic chlorides are formed, and if these are boiled repeatedly with water, they are converted into the trioxide, this reaction taking place more quickly in the presence of sodium carbonate. If antimony oxide be dissolved in boiling antimony trichloride, a pearl-grey, crystalline mass is obtained on cooling, having the composition $SbOCl,7SbCl_3$, and this compound yields the substance $2SbOCl,Sb_2O_3$ on treatment with absolute alcohol.

Antimony Pentachloride, $SbCl_5$, was discovered by H. Rose in 1835, and is prepared by the direct union of antimony and chlorine, which takes place with evolution of light and heat. It is also readily formed by saturating the fused trichloride with chlorine gas. Antimony pentachloride is a yellow, fuming, disagreeably-smelling liquid, which solidifies in a freezing mixture, forming crystals melting at −6°. It is readily volatile, partially decomposing on distillation into chlorine and trichloride, but under a pressure of 22 mm. it boils without decomposition at 79°, whilst under the same conditions the trichloride boils at 113·5°.[2] The vapour density[3] under a pressure of 58 mm. at 218° is 10, the calculated number being 10·3. When brought in contact with the requisite quantity of ice-cold water it forms the monohydrate,[4] $SbCl_5,H_2O$, crystallising from chloroform in thin, deliquescent scales melting at 90°. If more water be added[5] a clear liquid is obtained, and this, on standing over sulphuric acid, deposits crystals of $SbCl_5,4H_2O$, which are

[1] Sabanajew, *Zeit. Chem.*, 1871, 204.

[2] Anschütz and Evans, *Ber.*, 1886, **19**, 1994; *Journ. Chem. Soc.*, 1886, **49**, 708.

[3] Anschütz and Evans, *Annalen*, 1889, **253**, 95.

[4] Anschütz and Evans, *Annalen*, 1887, **239**, 239.

[5] Weber, *Annalen*, 1863, **125**, 86.

insoluble in chloroform (Anschütz and Evans). Hot water produces antimonic acid. As it easily loses chlorine, antimony pentachloride is employed in organic chemistry in the chlorination of many bodies, since by its successive formation and decomposition it acts as a chlorine carrier. With hydrocyanic acid it forms the white, crystalline compound $SbCl_5,3HCN$ which volatilises under 100° with partial decomposition. It also forms solid compounds with various chlorides, oxides, etc., such as $SbCl_5,SCl_4$; $SbCl_5,PCl_5$; $SbCl_5,POCl_3$; $2SbCl_5,5NOCl$; $2SbCl_5,NO$; $3SbCl_5,2NO_2$; $SbCl_5,N_4S_4$.

Antimony pentachloride forms a very large number of double salts, many of which are derived from the complex *metachloroantimonic acid*, $HSbCl_6$, which is obtained in greenish-yellow prisms containing $4\frac{1}{2}H_2O$ by the action of chlorine and hydrogen chloride on a solution of antimony trichloride.[1]

When three molecules of antimony pentachloride are heated with one molecule of pentoxide to 140° two oxychlorides are obtained, viz., Sb_3OCl_{13} and $Sb_3O_4Cl_7$, which as they melt at different temperatures can be separated one from the other. The first is a white, crystalline, extremely deliquescent mass, which melts at 85°, whilst the other forms yellowish crystals, melting at 97·5°.

Antimony Tetrachloride, $SbCl_4$, is not known in the free state, but it is probably present in the dark brown solution formed by the action of chlorine on an excess of antimony trichloride. A number of salts have been prepared of the type M'_2SbCl_6 which appear to be derived from the tetrachloride and are characterised by their dark colour. They are isomorphous with the corresponding salts of the tetrachlorides of lead, tin, and platinum.[2] The *rubidium salt*, Rb_2SbCl_6, is obtained by adding rubidium chloride to a mixture of equal molecular proportions of the tri- and penta-chlorides of antimony in presence of hydrochloric acid. It crystallises in lustrous dark violet, microscopic octahedra, and is decomposed by water. Analogous bromine compounds appear also to exist.

Antimony Tribromide, $SbBr_3$.—Powdered antimony combines directly with bromine with evolution of light and heat. The tribromide sublimes in colourless, deliquescent needles, which

[1] Weinland and Schmid, *Zeit. anorg. Chem.*, 1905, **44**, 37. See also *Ber.*, 1901, **34**, 2633; 1903, **36**, 244.

[2] Setterberg, *Ofver. K. Vetensk. akad. För.*, 1882, 23; Weinland and Feige, *Ber.*, 1903, **36**, 259; Weinland and Schmid, *Ber.*, 1905, **38**, 1080.

melt at 95° and boil at 275°; water decomposes it with formation of a basic bromide. Another method of preparation consists in heating an excess of powdered antimony with a solution of bromine in carbon disulphide; the tribromide thus obtained on evaporation crystallises in octahedra.

A pentabromide does not appear to exist.

Antimony Tri-iodide, SbI_3.—These elements combine together directly with evolution of so much heat that if large quantities are employed explosions may ensue. The tri-iodide is thus obtained as a brownish-red, crystalline mass, yielding a cinnabar-red powder, and crystallising in six-sided tablets from solution in hot carbon disulphide. It melts at 171° to a garnet-red liquid and forms a violet-red vapour, which at a higher temperature becomes scarlet. It sublimes at a temperature slightly above its melting point, boils between 414° and 427° (Carnelley and Williams), and is decomposed by water, with formation of a yellow oxyiodide, which forms crystalline double salts with the various iodides.

Both the bromide and iodide form numerous double salts.

Antimony Pentiodide, SbI_5, was supposed to be formed as a very unstable, brown, crystalline mass when the two elements were fused together and the excess of iodine removed by heating at 130°,[1] but its existence is very doubtful,[2] and Jaeger and Doornbosch[3] and also Quercigh[4] have shown by the method of thermal analysis that there is no evidence of its formation.

Antimony and the Sulphur Group.

452 Only two well-defined sulphides of antimony, the trisulphide, Sb_2S_3, and the pentasulphide, Sb_2S_5, are known. A tetrasulphide, Sb_2S_4, has been described, but its existence is doubtful.[5]

Antimony Trisulphide, Sb_2S_3, occurs crystallised as stibnite in the older stratified rocks. This is the most important ore of antimony, and it is found in considerable quantity, occurring in Cornwall, Hungary, Transylvania, in the Banat, in the Harz,

[1] Pendleton, *Chem. News*, 1883, **48**, 97.

[2] MacIvor, *Chem. News*, 1874, **29**, 255; *Journ. Chem. Soc.*, 1876, **29**, 330; *Chem. News*, 1902, **86**, 223.

[3] *Zeit. anorg. Chem.*, 1912, **75**, 261.

[4] *Atti R. Accad. Inst. Veneto Sci.*, 1912, **70**, ii. 667.

[5] See Bošek, *Journ. Chem. Soc.*, 1895, **67**, 515.

in Westphalia, in the Black Forest, in Bohemia, in the Auvergne, in Estramadura, Algiers, Corsica, Siberia, Nevada, New Brunswick, in Japan, where it is found in magnificently large and perfect crystals, and in Borneo in large quantities. It crystallises in prisms, but is usually found in columnar or striated masses, which soil the fingers like graphite. It is easily pulverisable, and readily fusible, and has a specific gravity of 4·62. The crude sulphide occurring in commerce is obtained by melting the ore in the manner already described, and is sold in rounded masses having the form of the vessel in which the molten sulphide solidifies. It has a metallic lustre, steel-grey streak, and crystalline fracture. From early times this substance has been used in the East under the name of Kohl. The alchemists occupied themselves much with the properties of this body, as it was used for the purification of gold, and was termed *judex ultimus* or *lupus metallorum*. Antimony trisulphide also exists in the amorphous state, and in this form was known to "Basil Valentine." He states that crude spiessglas may be sublimed with formation of a red body when it is mixed with *sal ammoniacum*. In this way antimony chloride and ammonium sulphide are formed, which again react on cooling, producing the original compounds, the antimony sulphide separating out as a red powder. Glauber, and also Lemery, speak of the solution and the subsequent precipitation of the spiessglas with caustic alkalis; but it was not until 1714 that attention was directed to the red sulphide of antimony. In this year a Carthusian monk whose life had been despaired of by the Paris faculty was saved by a monk of the name of Simon administering to him a medicine which was first prepared by a German apothecary, a disciple of Glauber, and which was bought by the Parisian apothecary de la Ligérie. This was soon known as the "poudre des chartreux," or Carthusian powder. Simon, however, gave to it the name of *Alkermes mineral*, and such was the reputation which this medicine enjoyed that the French Government bought the receipt for its preparation in 1720 from de la Ligérie. The process consisted in boiling the spiessglas with potashes and allowing the clear solution to cool, when the kermes was deposited as a red powder. In 1728 Stabel found that when caustic potash was employed, a red powder was also obtained, which Mender in 1738 showed to be pure kermes, and C. J. Geoffroy in 1735 proved that the same preparation

was obtained when spiessglas was fused with carbonates of the alkali metals, and the liver of antimony thus obtained boiled with water. This body was believed to be a compound of antimony, sulphur, and alkali, though chemists such as Baumé denied that it contained any alkali, and assumed that in spiessglas regulus of antimony was combined with sulphur, whilst in mineral kermes calx of antimony was combined with sulphur. Many other views were held concerning the composition of this compound until Rose in 1825, and Fuchs in 1833, showed that mineral kermes is nothing more than amorphous antimony sulphide.

Various methods may be adopted for the preparation of mineral kermes, which for fifty years was highly prized as a medicine, and even now is sometimes employed. All these processes yield a preparation containing, as impurity, varying quantities of antimony oxide, both free and combined with the alkalis, and moreover on exposure to air oxidation occurs with formation of the oxide and free sulphur.[1] Hence the preparation of the kermes should be carried on exactly according to the prescription of the pharmacopœia.

In order to prepare the amorphous sulphide free from oxide, the crystalline compound is boiled with caustic potash in absence of air, the liquid filtered and the hot diluted solution precipitated with sulphuric acid. The precipitate is then washed with very dilute acid, and afterwards with cold water; and to remove any oxide which may be present it is heated with a solution of tartaric acid. Thus obtained the precipitate becomes anhydrous when dried at 100° and forms a reddish-brown light powder which readily soils the fingers. This is more soluble in hydrochloric acid, in the fixed alkalis and their carbonates than the crystalline compound into which it is converted on fusion. It may also be obtained by pouring fused stibnite into an excess of cold water. It then forms an amorphous lead-grey mass which appears of a hyacinth-red colour when seen in thin films, has a specific gravity of 4·15, and when triturated is converted into a dark reddish-brown powder.

If sulphuretted hydrogen is passed into an acid solution of the trichloride or into an acidified solution of tartar emetic, an orange-red precipitate of amorphous hydrated sulphide is obtained, which after drying at 100–130° becomes black at 200°. The precipitated sulphide also becomes black when it is boiled

[1] Pollacci, *Boll. Chim. Farm.*, 1906, **45**, 401.

with two parts of hydrochloric acid and one of water in a current of carbon dioxide.[1]

When the sulphide is heated at 850° in nitrogen, and the vapours rapidly condensed, black needles are formed accompanied by lilac-coloured spherical globules which appear to constitute a polymorphic variety of the sulphide.[2] This form has the specific gravity 4·278 at 0°, and passes at 220° into the black crystalline form, which has the specific gravity 4·652 and melts [3] at 540°.

When a dilute solution of tartar emetic is added to sulphuretted hydrogen water a colloidal solution of antimony sulphide is produced, which is orange-red by transmitted light, and can be boiled without undergoing change. Calcium chloride and many other electrolytes cause an immediate precipitation of the sulphide.[4] On heating in a current of hydrogen the trisulphide is reduced to metal, but it may be sublimed without decomposition in an atmosphere of nitrogen. The equilibrium between the sulphide and hydrogen at various temperatures has been examined by Pélabon.[5] Crystalline antimony sulphide is used not only for the preparation of the other antimony compounds, but also in pyrotechny, and for the preparation, especially in Sweden, of the heads of lucifer matches, as well as for the composition used for firing breechloading firearms. The amorphous sulphide is largely used as a means for vulcanising caoutchouc, to which it also imparts a reddish-brown colour.

The compound known as *antimony cinnabar*, which is obtained by warming a solution of the trichloride with sodium thiosulphate, is the trisulphide. This substance is used in oil painting as well as in water-colour painting and as a distemper.

The Thioantimonites or *Livers of Antimony* are formed by the combination of the trisulphide with metallic sulphides.[6] Those of the alkali metals are prepared by fusing the constituents together. They are brown or black, and when they contain a large quantity of metallic sulphide they are easily soluble in

[1] Mitchell, *Chem. News*, 1893, **67**, 291.

[2] Guinchant and Chrétien, *Compt. rend.*, 1904, **138**, 1269; **139**, 51.

[3] See also Pélabon, *Compt. rend.*, 1904, **138**, 277; and Zani, *Bull. Acad. roy. Belg.*, 1909, 1169.

[4] Picton, *Journ. Chem. Soc.*, 1892, **61**, 142; Biltz and Geibel, *Nachr. K. Ges. Wiss. Göttingen*, 1906, 141.

[5] *Compt. rend.*, 1900, **130**, 911.

[6] See Pouget, *Compt. rend.*, 1897, **124**, 1445, 1518.

water, but when the quantity of antimony increases, these livers of antimony become more sparingly soluble, and at last insoluble in water. The same compounds are formed when the trisulphide is dissolved in an aqueous solution of a sulphide, or, mixed with antimonite, when the trisulphide is fused with an alkali or alkali carbonate or treated with the solution of an alkali:

$$2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O.$$

Acids precipitate the amorphous trisulphide from these solutions, which also absorb oxygen rapidly from the air. Many of the thioantimonites occur as minerals, and the composition of some of these has been already given.[1] The alkali salts [2] belong to the types $MSbS_2$, M_3SbS_3, $M_2Sb_4S_7$, and $M_4Sb_2S_5$.

Antimony Pentasulphide, Sb_2S_5.—This compound does not occur in the native state. "Basil Valentine" mentions that when spiessglas is boiled with strong caustic ley, and acetic acid added to the liquor, a red body is precipitated, and Quercetanus in 1603 mentions in his pharmacopœia a preparation from spiessglas and liver of sulphur by means of acids, terming it *sulphur antimonii auratum*. In 1654 Glauber mentions in the "pharmacopœia spagyrica" the preparation obtained by precipitating the slag formed in the preparation of regulus of antimony by means of acetic acid, and recommends this product as *panacea antimonialis* or *sulphur purgans universale*. This preparation, which was known as golden sulphuret of antimony, soon became a favourite medicine. It was obtained from the more or less oxidised solution of liver of antimony, containing a thioantimonate. If this be fractionally precipitated by hydrochloric acid a brown kermes is first thrown down and afterwards a golden-coloured sulphide, which has therefore been termed *sulphur auratum tertiæ præcipitationis*. In later times stibnite was boiled with alkali with addition of sulphur and the solution precipitated with acid. At the present day pure thioantimonate is first prepared, and for this purpose the well-crystallised sodium salt is employed; this is dissolved in from 10 to 60 parts of water and a cold mixture of 3·3 parts of sulphuric acid and 100 parts of water is gradually added; the precipitate

[1] See also Sommerlad, *Zeit. anorg. Chem.*, 1897, **15**, 173; Pouget, *Compt. rend.*, 1897, **124**, 1518; 1903, **136**, 1450.

[2] See Pouget, *Compt. rend.*, 1897, **124**, 1445; 1898, **126**, 1144, 1792. Stanek, *Zeit. anorg. Chem.*, 1898, **17**, 117.

is well washed with distilled water and dried at a moderate temperature in the dark.

The pure pentasulphide is precipitated when an excess of sulphuretted hydrogen water is added to a solution containing the antimony in the form of antimonic acid at the ordinary temperature (Bunsen).[1] When sulphuretted hydrogen is passed into the antimony solution a mixture of pentasulphide, trisulphide, and sulphur is formed, the proportion of the pentasulphide diminishing as the rate at which the gas is passed is lessened and as the temperature is raised. Hydrochloric acid up to about 20 per cent. favours the production of the pentasulphide, but in larger amount hinders it.[2]

Antimony pentasulphide is a fine yellowish-red powder easily soluble in aqueous alkalis and their sulphides, and also, in absence of air, in warm ammonia. It likewise dissolves in the carbonates of the alkali metals, but not in ammonium carbonate. When exposed to sunlight, heated in water to 98°, or simply heated in absence of air, it decomposes into the black trisulphide and sulphur, and when boiled with hydrochloric acid, sulphur separates out, sulphuretted hydrogen is evolved, and the trichloride is found in solution.

Sodium Thioantimonate, $Na_3SbS_4,9H_2O$.—This is termed, from the discoverer, *Schlippe's salt*, and is obtained by dissolving the trisulphide, sulphur, and caustic soda or a mixture of soda-ash and lime, in the requisite quantity of water; or by fusing together 16 parts of anhydrous sodium sulphate, 13 parts of stibnite, and 5 parts of carbon, dissolving, and boiling the solution with 2·5 parts of sulphur. It crystallises in large, colourless or yellow, regular tetrahedra which have an alkaline reaction and a saline cooling metallic taste resembling that of liver of sulphur. It dissolves at 15° in 2·9 parts of water and is precipitated from aqueous solution by alcohol. The hydrated crystals on exposure to moist air soon become covered with a kermes-coloured coating, and when they are heated in absence of air water is given off and the anhydrous salt formed. This fuses at a dark-red heat, yielding on solidification a soluble brown mass.

Potassium Thioantimonate, $K_3SbS_4,9H_2O$, is prepared in a similar way to the sodium salt and forms deliquescent crystals.

[1] *Annalen*, 1878, **192**, 305.

[2] Bošek, *Journ. Chem. Soc.*, 1895, **67**, 515; Brauner, *ibid.*, 527. See also Klenker, *J. pr. Chem.*, 1899, [2], **59**, 150, 353.

Ammonium Thioantimonate, $(NH_4)_3SbS_4$, is formed when the trisulphide and flowers of sulphur are dissolved in red ammonium sulphide. It crystallises in unstable pale yellow prisms.[1]

Barium Thioantimonate, $Ba_3(SbS_4)_2,6H_2O$, is prepared by dissolving the freshly precipitated golden sulphide of antimony in barium monosulphide and precipitating by alcohol. In this way stellate groups of needles are obtained.

The *calcium* salt is prepared in a similar way and is thrown down as an oily liquid on addition of alcohol.

The thioantimonates of the alkali metals have been isolated by Donk.[2]

The thioantimonates of the other groups are almost entirely insoluble in water and are obtained by double decomposition between their soluble salts and sodium thioantimonate. They are yellow, red, brown, or black precipitates.

Antimony Oxysulphide, Sb_2S_2O, is found, together with stibnite, as kermesite or antimony blende in needle-shaped crystals or thin six-sided prisms which have a cherry-red colour and an almost metallic lustre. The same compound is obtained as a reddish-brown powder by adding antimony trisulphide to fused antimony iodide, and treating the mass with dilute hydrochloric acid, when a dark reddish-brown lustrous powder of antimony thio-iodide, SbSI, remains behind, and this, when boiled with water and oxide of zinc, is converted into the oxysulphide.

Both the following preparations, which were formerly made use of, are probably mixtures of the oxide and sulphide, as was shown by Proust in opposition to the view held by Berthollet that they were compounds of the oxide with varying amounts of sulphur.

Glass of Antimony or *Vitrum Antimonii* is obtained by fusing oxidised stibnite with a small quantity of the sulphide. It forms a transparent dark ruby-red mass, formerly largely employed for obtaining the other antimony compounds, but now used only for imparting a yellow tint to glass and porcelain.

Antimonial Saffron or *Crocus Antimonii*.—If stibnite is deflagrated with a quantity of saltpetre insufficient for complete oxidation a brownish-yellow powder is obtained on lixiviation which when heated melts to a yellow glass.

[1] Stanek, *Zeit. anorg. Chem.*, 1898, **17**, 117.
[2] *Chem. Weekblad*, 1908, **5**, 529, 629.

Chlorosulphide of Antimony.—Two compounds of this class, SbS_2Cl and Sb_2S_5Cl, have been obtained as reddish-brown crystalline substances by the action of sulphuretted hydrogen on antimony trichloride at its melting point.[1] The compound $SbSCl,7SbCl_3$ is obtained by heating the trichloride and trisulphide together. Alcohol converts it into $2SbSCl,3Sb_2S_2$.

Iodosulphide of Antimony.—Compounds of the formulæ SbS_2I and SbS_2I_3 are formed when antimony trisulphide is heated with iodine (Ouvrard).

Antimony Trisulphate, $Sb_2(SO_4)_3$, is obtained as a white mass by heating either the metal or the oxide with concentrated sulphuric acid. The composition of the salt depends on the concentration of the acid used, acid or basic salts being obtained when the acid employed is stronger or weaker than that represented by the formula H_2SO_4.[2] The normal salt crystallises from a tolerably acid concentrated solution in long glistening silky needles,[3] and is decomposed by water into a soluble acid salt, and an insoluble basic salt. If antimony chloride be heated with fuming sulphuric acid a basic salt, $Sb_2O(SO_4)_2$, is produced in small glistening crystals, which in contact with alcohol are transformed into the salt $Sb_2O_2SO_4$, consisting of a white powder, which, when treated with boiling water, yields the salt $Sb_4O_5SO_4$. Several other salts have also been described.

Antimony sulphate yields double salts with the alkali sulphates, such as $KSb(SO_4)_2$, which crystallises in nacreous leaflets. These are decomposed by water, yielding antimonious hydroxide.[4]

453 *Antimony Triselenide,* Sb_2Se_3, is formed when the two elements are fused together, a metallic lead-grey crystalline mass being produced[5] which melts at 605°. When selenium hydride is passed into a solution of tartar emetic the same compound is precipitated as a black powder.

Antimony Pentaselenide, Sb_2Se_5, is precipitated as a brown powder by adding dilute sulphuric acid to a solution of sodium seleno-antimonate.

[1] Ouvrard, *Compt. rend.*, 1893, **116**, 1516; **117**, 107.

[2] Adie, *Chem. News*, 1890, **61**, 58.

[3] Schultz-Sellack, *Ber.*, 1871, **4**, 13.

[4] Gutmann, *Arch. Pharm.*, 1898, **236**, 477; Metzl, *Zeit. anorg. Chem.*, 1906, **48**, 140; German Patent 161776. See also Kühl, *Zeit. anorg. Chem.*, 1907, **54**, 256; Gutmann, *Arch. Pharm.*, 1908, **246**, 187.

[5] See Pélabon, *Compt. rend.*, 1906, **142**, 207; Chrétien, *ibid.*, 1339, 1412.

Sodium Seleno-antimonate, $Na_3SbSe_4 9H_2O$, is isomorphous with the corresponding thio-antimonate, and is obtained by fusing together 4 parts of sodium carbonate, 6 parts of antimony triselenide, 3 parts of selenium, and 1 of charcoal. The fused mass is boiled out with water in absence of air and the filtrate covered with a layer of strong alcohol. The salt separates out after some time in orange-red transparent tetrahedra which are soluble in two parts of cold water and become red-coloured on exposure to air, with separation of selenium. When a solution of Schlippe's salt is boiled with selenium, filtered, and the solution concentrated in absence of air, yellow tetrahedra of $Na_3SbSeS_3,9H_2O$ are deposited.

Antimony and tellurium [1] when fused together yield only one definite compound, *antimony tritelluride*, Sb_2Te_3.

Antimony and the Nitrogen Group.

454 No definite nitrate of antimony is known, although the white powder obtained by the action of nitric acid on antimony contains nitrogen, and is converted by water into antimony pentoxide and nitric acid.

If phosphorus be added to fused antimony a tin-white *phosphide of antimony* is obtained which when heated in the air burns with a greyish flame.

Antimony Thiophosphate, $SbPS_4$ or Sb_2S_3,P_2S_5, is formed when the trichloride or trisulphide is heated with phosphorus pentasulphide. It is a fusible, insoluble, yellow, crystalline mass.[2]

Antimony combines directly with arsenic. The compound $SbAs_3$ occurs as allemontite in reniform or amorphous masses having a metallic lustre.

Medicinal Uses of Antimony.

455 As we have seen, various antimony preparations are used as important medicines. Paracelsus was one of the first to employ these for internal use, and his example was followed by the other iatro-chemists, many of whom worked diligently on antimony and its compounds. The disciples of the old Galenic school were violently opposed to the introduction of the antimony compounds into medicine, and they succeeded in

[1] See Fay and Ashley, *Amer. Chem. J.*, 1902, **27**, 95.

[2] Glatzel, *Ber.*, 1891, **24**, 3886.

inducing the Paris Parliament in 1566 to prohibit the use of antimony and its compounds by all physicians on pain of having their licences withdrawn. In 1603 the medical faculty of Paris took a similar step, and this decree was not withdrawn until the year 1666.

Metallic antimony itself was at one time employed for the preparation of goblets in which wine was allowed to stand overnight in order that it might be used as an emetic ; but this practice fell into disuse even during Boyle's time. Pills made of metallic antimony were employed at a later period; these were termed everlasting pills, because they, like the goblets, were believed only to act by contact and not to lose their weight. This error was first combated by Lemery and Vigani, a Veronese quack doctor who lived in England, and they showed that both antimony and fused stibnite became acted upon when placed in contact with wine.

Whilst formerly a large number of antimony compounds were employed in medicine, the only ones which are used at the present day are tartar emetic or potassium antimonyl tartrate, $C_4H_4K(SbO)O_6$, and the trisulphide or *antimonium sulphuratum*. The first compound is given in doses of 0·0027 to 0·008 gram as a diaphoretic, and from 0·065 to 0·13 gram as an emetic. The dose of the second is from 0·065 to 0·13 gram.

In larger doses it produces, like white arsenic, violent irritation in the intestines, vomiting and purging. When one large dose only is administered the case proceeds rapidly to recovery or death, generally the former, if the case be placed early under proper treatment, and in this respect acute antimonial is distinguished from acute arsenical poisoning.

In cases of chronic antimony poisoning the principal symptoms are dryness of the throat, pain on swallowing, nausea and vomiting, diarrhœa, loss of flesh, giddiness, fainting, and albuminuria. Death takes place from exhaustion and wasting. Several cases have occurred in this country to show that tartar emetic has been thus criminally and fatally used (Taylor).

Detection and Estimation of Antimony.

456 When a small quantity of an antimony compound is heated in the upper reduction zone of a Bunsen burner on a thread of asbestos the flame becomes of a bluish tinge, and when a small porcelain basin filled with cold water is held

above it a brownish-black deposit of metallic antimony is found upon the basin, and this is but slightly attacked by cold nitric acid, and is insoluble in sodium hypochlorite. Arsenic gives a very similar reaction, but this may be distinguished from antimony by the fact that during the reduction a garlic-like smell of arsenic is noticed, and that the metallic film is readily soluble in sodium hypochlorite. If an antimony compound is heated on a carbonised match a brittle metallic bead is obtained, whilst arsenic is completely volatilised. Most of the antimony compounds are insoluble in water but dissolve in hydrochloric acid. Those which do not thus dissolve may be obtained in solution by fusion with potassium carbonate and saltpetre, and subsequent solution in hydrochloric acid. Sulphuretted hydrogen produces in acid solutions a very characteristic orange-red coloured precipitate of antimony trisulphide. If other metals precipitable by sulphuretted hydrogen are present, the mixed sulphides, after washing, are treated with ammonium sulphide, filtered, and the filtrate acidified with hydrochloric acid. This precipitate may contain, together with antimony, the sulphides of tin and arsenic. This last metal is removed by digesting with freshly prepared solution of ammonium carbonate, and washing the residue with water. This is then brought into solution by heating with hydrochloric acid, and the liquid is placed in a platinum dish containing a piece of zinc; the antimony is deposited upon the platinum as a black adherent coating, which is readily soluble in nitric acid and can then be identified as antimony. A more satisfactory method consists in dissolving the mixed sulphides in caustic soda and a few drops of yellow ammonium sulphide and then boiling with sodium peroxide, which converts the metals into stannate, antimonate, and arsenate respectively. Tin is then detected by boiling with ammonium chloride, which precipitates stannic hydroxide, and arsenic and antimony are detected in the acidified filtrate by Bunsen's method described below.[1] A rapid method of detection is to boil the sulphides with a 5 per cent. solution of sodium carbonate, which leaves tin sulphide undissolved, and yields a solution which deposits antimony sulphide on cooling, whilst arsenic sulphide remains dissolved and can be detected as usual.[2]

[1] Walker, *Journ. Chem. Soc.*, 1903, **83**, 184.

[2] Materne, *Bull. Soc. chim. Belg.*, 1906, **20**, 46.

Antimony may also be detected by means of Marsh's test carried out as described under arsenic (Vol. I., p. 710). The mirror obtained is deposited much closer to the flame than that of arsenic, is formed at a lower temperature, does not yield a crystalline deposit of oxide when heated in the air, and is not soluble in sodium hypochlorite. When the gas is passed into silver nitrate solution, silver antimonide is precipitated (p. 973).

Antimony trichloride gives a spark spectrum containing among others the following lines, mentioned in order of their relative brightness (Lecoq de Boisbaudran):

α 6005 β 5568 γ 6130 δ 6079

Antimony is usually estimated gravimetrically either as the sulphide or the tetroxide. In the first case it is obtained as a hydrated precipitate, which may also contain sulphur and pentasulphide. It is necessary, therefore, to dry this at 100°, to weigh it, and to bring a known fraction into a porcelain boat contained in a glass tube. Through the tube dry carbon dioxide is passed, and the sulphide is heated, the pure anhydrous trisulphide remaining behind. The sulphide may also be oxidised by means of nitric acid and the residue ignited and weighed as tetroxide, or it may be dissolved in a large excess of sodium sulphide, potassium cyanide added, and the resulting solution electrolysed and the metal weighed.[1] Antimony is also frequently estimated volumetrically, the trioxide, in presence of sodium bicarbonate, being converted by means of standard iodine solution into the pentoxide, or the trichloride being converted into the pentachloride by a standard solution of sodium bromate in presence of hydrochloric acid.[2]

The *quantitative* separation of antimony from other metals, with the exception of arsenic and tin, does not exhibit any difficulty. Should these three elements be present together their sulphides must be first converted into oxides by treatment with nitric acid, and these fused for some time with eight times their weight of caustic soda. The cooled mass is next allowed to soften in hot water until the sodium metantimonate has separated out as a white powder, and then one volume of alcohol of specific gravity 0·83 is added for every three volumes of the liquid. After standing for some time the liquid is filtered

[1] Kohn and Barnes, *British Assoc. Reports*, 1896, 244. See also Law and Perkin, *Trans. Faraday Soc.*, 1905, **1**, 262.

[2] Nissenson and Siedler, *Chem. Zeit.*, 1903, **27**, 749; Rowell, *J. Soc. Chem. Ind.*, 1906, **25**, 1181.

and the precipitate well washed with dilute alcohol, to which at last some caustic soda is added. The filtrate contains the stannate and arsenate, whilst the whole of the antimony is contained in the residue, and this is converted in the usual way into the sulphide (H. Rose). A more rapid method of separation depends on the fact that in presence of free oxalic acid antimony is precipitated by sulphuretted hydrogen as the sulphide, whereas tin remains in solution.[1] Antimony and tin can also be separated electrolytically.[2]

The separation of antimony from arsenic, which had previously been difficult and unsatisfactory, was first rendered exact by Bunsen. The moist and well-washed mixture of sulphides obtained by precipitation with sulphuretted hydrogen is dissolved on the filter in an excess of caustic potash, and the diluted solution treated with chlorine until all the free alkali has combined. The excess of chlorine is then got rid of by repeated evaporation with hydrochloric acid, the solution diluted, and this treated with a freshly prepared solution of sulphuretted hydrogen until all the antimony is precipitated. A rapid current of air is then passed through the liquid in order to expel the excess of sulphuretted hydrogen, and the precipitate washed first with water, then with alcohol, and at last repeatedly with carbon disulphide, in order to remove free sulphur. After drying at 110°, pure pentasulphide of antimony remains, and this is afterwards weighed. The arsenic in the filtrate may be estimated by subsequent continued treatment with sulphuretted hydrogen when the pentasulphide is precipitated and treated as above described.

A still simpler method of effecting this separation consists in adding ferrous sulphate or chloride to a solution of the chlorides of the two metals in hydrochloric acid, saturating with hydrochloric acid gas and distilling. The whole of the arsenic passes over and may be collected in dilute hydrochloric acid, whilst the antimony remains behind and may be precipitated in the usual way after the ferric salt has been reduced to the ferrous state.[3]

[1] Clarke, *Chem. News*, 1870, **21**, 124; Lesser, *Zeit. anal. Chem.*, 1888, **27**, 218; Warren, *Chem. News*, 1890, **62**, 216; Clark, *Journ. Chem. Soc.*, 1892, **61**, 424; Henz, *Zeit. anorg. Chem.*, 1903, **37**, 1.

[2] See Fischer, *Zeit. anorg. Chem.*, 1904, **42**, 363, where the literature of the subject is quoted. Compare Cohen and Morgan, *Analyst*, 1909, **34**, 3.

[3] Fischer, *Ber.*, 1880, **13**, 1778. See also Piloty and Stock, *Ber.*, 1897, **30**, 1649; Beck and Fisher, *Chem. News*, 1899, **80**, 259, where a critical discussion of the various methods is to be found.

Atomic Weight.—The methods which have at various times been employed for the determination of the atomic weight of antimony have led to somewhat divergent results. The number 129, which was obtained by Berzelius by the oxidation of the metal with nitric acid, was long accepted as correct, until Schneider's experiments[1] on the reduction of the sulphide proved that 120·55 was nearer the truth. Dexter[2] then found the number 122·4 by the treatment of the metal and trioxide with nitric acid, the resulting oxide being converted into the tetroxide by ignition. This was confirmed by Kessler,[3] who adopted the same plan, but effected the oxidation volumetrically by means of an acid solution of potassium chlorate, and by Dumas,[4] who analysed the trichloride. On the other hand, a very carefully conducted series of analyses of the bromide led Cooke[5] to the number 119·86. The electrolysis of the chloride led in the hands of Pfeiffer[6] and of Popper[7] to the number 121·2, but it has been shown that the method applied is not accurate.[8]

Finally, a series of determinations made by Friend and Smith,[9] by the indirect method of heating potassium antimony tartrate in hydrogen chloride and weighing the potassium chloride produced, gave the number 120·34.

The value at present (1913) adopted is 120·2.

BISMUTH. Bi = 208·0.

457 The word *marcasite*, by which, up to recent times, the metal bismuth was often designated, is found in the authors of the thirteenth century. Hence it has been supposed that this metal was known at that time. This is, however, not the case, for the name marcasite had in those days, and even at a much later period, a very indefinite meaning, being given to any ore which had a metallic appearance, and especially to those ores which are now classed as pyrites.

Bismuth was classed by Paracelsus amongst the semi-metals.

[1] *Pogg. Ann.*, 1856, **98**, 293.
[2] *Pogg. Ann.*, 1857, **100**, 563.
[3] *Pogg. Ann.*, 1861, **113**, 145.
[4] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.
[5] *Amer. J. Sci.*, 1878, **15**, 41, 107; 1880, **19**, 382.
[6] *Annalen*, 1881, **209**, 173.
[7] *Annalen*, 1886, **233**, 153.
[8] Cohen and Strengers, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, **5**, 543.
[9] *J. Amer. Chem. Soc.*, 1901, **23**, 502.

On the other hand, Agricola mentions *bisemutum* or *plumbum cinereum* as a true metal which is usually added to tin in order to make it work better. Notwithstanding this clear statement, it was subsequently confounded by Libavius with antimony, and by Lemery with zinc. Metallic bismuth was moreover described by "Basil Valentine" in his Last Testament: "Antimonium must be placed between tin and lead, as bismuth or magnesia is placed under and between tin and iron," and he also states that "bismuth or marcasite is a bastard *jovis*." Pott, in 1739, was the first to make us acquainted with the special properties of bismuth, and its reactions were exactly studied by Bergman.

Bismuth is a comparatively rare metal. It is found chiefly in the native condition, but also as the oxide or bismuth ochre, Bi_2O_3; less frequently it occurs as bismuthite, Bi_2S_3, whilst it is found still more sparingly in the following minerals: telluric bismuth or tetradymite, $Bi_2(Te,S)_3$; emplectite, $Cu_2Bi_2S_4$; bismutite, $3(BiO)_2CO_3.2Bi(OH)_3.3H_2O$; aikinite, $Bi_2S_3.2PbS,Cu_2S$; bismutosmaltite, $Co(As,Bi)_2$; pucherite, $BiVO_4$; eulytite or bismuth silicate, $Bi_4(SiO_4)_3$, &c., and occurs in traces in the pyrites of Agordo. Native bismuth is sometimes found nearly pure. Usually, however, it contains other metals alloyed with it, or it is mixed with a variety of ores. Bismuth is found in veins traversing gneiss or clayey slate in Bolivia, Saxony, Australia, &c., and is usually associated with ores of silver and cobalt.

458 *The Metallurgy of Bismuth.*—Formerly bismuth was obtained by simply heating the ore in sloping iron tubes. In this way merely that portion of the metal present in the native state was obtained, and this only in a very incomplete manner. The residue was employed in the manufacture of smalt, and the bismuth again extracted from the cobalt speiss.

At the present day the liquation process has been superseded, except for the treatment of ores containing native bismuth, by smelting methods. Oxidised ores may be treated direct, but sulphides must be subjected to a preliminary roast. Reduction is carried out in small crucible furnaces or in reverberatory furnaces, the charge being made up of ore, carbon, slag, sodium carbonate, limestone, and sometimes fluorspar. It is essential to have an easily fusible slag so as to avoid loss by volatilisation. The products of this operation are generally crude bismuth,

matte or speiss, and slag. For ores carrying sulphide of antimony and arsenic some scrap iron is added to the charge in addition to the fluxes already mentioned.

Bismuth is also extracted by wet methods from ores and products containing the oxide and carbonate. These are first treated with hydrochloric acid, and the bismuth is afterwards precipitated by means of iron, or the solution is largely diluted with water in order to precipitate the metal as oxychloride, which is collected, dried, and reduced.

The crude bismuth thus obtained generally contains lead, antimony and arsenic, besides traces of iron, cobalt, nickel, silver, and sulphur, and is subjected to a refining operation.

The bismuth is melted in small iron kettles under a cover of salt, potassium chloride, caustic soda and sufficient oxychloride of bismuth to take up the lead, which must be got rid of first. The mass must be constantly stirred, and in from one to three hours the whole of the lead is converted into chloride, and a corresponding amount of bismuth is separated from the oxychloride. Antimony is removed in the same way with a flux of soda, potash and sulphur, sodium thioantimonate being formed, whilst for arsenic the flux used is caustic soda and nitre.[1] A simple liquation process is often used for refining crude bismuth, the metal being melted on a slightly inclined iron plate.

The composition of commercial bismuth is seen from the following table.

Analyses of Commercial Bismuth.

	Saxon Bismuth.	Bismuth from Joachimsthal.	Peruvian Bismuth.
Bismuth	99·79	99·32	93·37
Iron	0·02	trace	2·058
Copper	0·03	trace	
Lead	0·08	0·30	—
Silver	0·07	0·38	—
Antimony	—	—	4·57
Tin	—	—	
Sulphur	—	—	—

[1] Borchers, *Mineral Industry*, 1899, **8**, 62.

Bismuth which contains 1 or more per cent. of lead melts at a lower temperature than pure bismuth. Such an impure metal exhibits on cooling the peculiarity that the solid crust of pure crystallised bismuth is seen to be broken through by drops of a liquid alloy, and this property has been employed to separate bismuth from lead (Matthey). Silver behaves in a similar manner. Commercial bismuth frequently contains small quantities of gold, which, along with silver, may be removed by melting with 2 per cent. of zinc and skimming off the surface layer, which is found to contain the precious metals.[1]

When bismuth is required for pharmaceutical purposes it is necessary to separate traces of arsenic which it sometimes contains. For this purpose it is melted with nitre or other oxidising agent, or fused with metallic iron. The arsenic is also removed when the molten metal is well stirred and exposed to the air, any antimony being simultaneously oxidised.[2]

Herapath,[3] who found a small quantity of thallium in certain bismuth preparations, recommends that the bismuth salts which are to be employed for medicinal purposes should be boiled with caustic soda solution, the residue well washed with water, dissolved in nitric acid, and the basic nitrate precipitated by the addition of an excess of water. From this the other preparations of the metal can be obtained.

In order to prepare chemically pure bismuth, the commercially pure metal is dissolved in nitric acid and evaporated with hydrochloric acid. The chloride is then dissolved in hydrochloric acid and the solution mixed with alcohol, which precipitates the greater portion of the lead in the form of chloride. The filtrate is poured into water and the precipitated oxychloride washed, redissolved in hydrochloric acid, and again precipitated with water, this process being frequently repeated. The oxychloride is then again dissolved in hydrochloric acid and precipitated with ammonia and ammonium carbonate, this operation being repeated three times, after which it is finally reconverted into oxychloride, and the latter reduced to metal by fusion with potassium cyanide. The metal thus obtained still contains lead, from which it can only be freed by electrolysis. For this purpose it is dissolved in nitric acid

[1] Matthey, *Proc. Roy. Soc.*, 1887, **42**, 89.
[2] Matthey, *Proc. Roy. Soc.*, 1893, **52**, 46.
[3] *Pharmaceutical Journal*, 1863, **4**, 302.

and the solution slowly electrolysed, any lead being deposited as peroxide on the positive pole. The bismuth is then finally fused with potassium cyanide.[1]

459 *Properties.*—Bismuth is a hard brittle metal, having a bright metallic lustre and a greyish-white colour, with a distinctly reddish tinge. Its specific gravity at 15° is 9·747 ; it melts at 270° and expands in the act of solidification, the specific gravity of the solid at the temperature of the melting point being 9·673 and that of the liquid 10·004.[2] Its boiling point lies in the neighbourhood of 1420° (Greenwood), and it can be distilled in a current of hydrogen. The vapour density between 1600° and 1700° is about 11, a number which is intermediate between the values corresponding to the formulæ Bi and Bi_2.[3] When a large quantity is melted, allowed to cool slowly until the surface begins to solidify, the crust then broken, and the liquid metal poured out, fine large crystals are obtained. These are obtuse rhombohedra which have the appearance of cubes as their angles approach closely to 90°. Acicular needles consisting of elongated hexagonal prisms have also been observed.[4] The crystals oxidise in the air, and frequently become covered with an iridescent film of oxide. The same colours may be obtained when the metal is melted in the air, but if the heat be continued, the metal gradually becomes altogether converted into oxide; at a red-heat steam is slowly decomposed by bismuth. This metal combines also directly with the elements of the chlorine group and with sulphur; hydrochloric and sulphuric acids do not act upon it in the cold, but the latter acid dissolves it on heating with evolution of sulphur dioxide. Hydrochloric acid dissolves it in the presence of dissolved oxygen. The best solvents for bismuth are nitric acid and aqua regia, both of which dissolve the metal readily in the cold.

Bismuth can be obtained in the colloidal form by reducing the nitrate by stannous chloride in the presence of ammonia and ammonium citrate,[5] or the oxychloride by hypophosphorous acid.[6]

Bismuth serves for the preparation of many pharmaceutical

[1] Classen, *Ber.*, 1890, **23**, 940.
[2] Vicentini, *Journ. Chem. Soc.*, 1891, **60**, 518.
[3] Meyer, *Ber.*, 1889, **22**, 726.
[4] Heberdey, *Sitzungsber. K. Akad. Wien*, 1895, **104**, i. 254.
[5] Lottermoser, *J. pr. Chem.*, 1899, [2], **59**, 489.
[6] Gutbier and Hofmeier, *Zeit. anorg. Chem.*, 1905, **44**, 225.

products and cosmetics, and is also employed for the manufacture of alloys of low melting point, and in the construction of thermopiles.

Alloys of Bismuth.

460 Bismuth forms a number of alloys of low melting point, which are known by the general name of fusible metal. The temperature of the melting point depends on the proportion of the constituents as is shown in the following table:

	Newton's Metal.	Rose's Metal.	Lichtenberg's Metal.	Wood's Metal.	Lipowitz.
Bismuth	8	2	5	4	15
Lead	5	1	3	2	8
Tin	3	1	2	1	4
Cadmium . . .	0	0	0	1	3
Melting point .	94·5°	93·75°	91·6°	71°	60°

The melting point can be still further lowered by the addition of mercury. Fusible metal is now largely used for stereotyping, obtaining copies of wood-cuts, &c., and is not only valuable on account of its low melting point, but also because it expands considerably in the act of solidification, and thus gives a perfect cast; it is important to make the cast when the metal is so far cooled that it is beginning to be viscid. If any of these liquid alloys be poured into a glass vessel this flies to pieces when the metal cools. Bismuth is also used in the manufacture of solder, and the soldering can be effected under hot water when a few drops of hydrochloric acid have been added. Alloys of lead, tin, and bismuth mixed together in such proportion that the mixture fuses at some particular temperature above 100° serve as safety-plugs for boilers and automatic sprinklers. Bismuth alloys, melting at a given temperature, are used for tempering steel; the pencils used for writing on the so-called metallic paper likewise consist of an alloy of bismuth.

Bismuth in very small quantities renders gold and silver brittle, and greatly diminishes the conductivity of copper for electricity.

Molten bismuth, to which 0·05 per cent. of tellurium has been added, solidifies to a minutely crystalline mass, entirely different in appearance, fracture, &c., from the pure metal.

When bismuth is treated with a solution of sodium in liquid ammonia a compound of the formula $BiNa_3$ is formed as a bluish-black mass, which takes fire in the air, and decomposes water with evolution of hydrogen.[1]

COMPOUNDS OF BISMUTH.

Bismuth and Oxygen.

461 Only two well-defined oxides of bismuth are known:
Bismuth suboxide or dioxide, BiO or Bi_2O_2.
Bismuth trioxide, Bi_2O_3.

The suboxide has only very feeble basic properties, whereas the trioxide is a well-marked basic oxide and corresponds to the stable salts of bismuth of the general formula BiR^I_3. Higher oxides are formed by the action of various oxidising agents on the trioxide, to which the formulæ Bi_2O_4 and Bi_2O_5 have been ascribed, but no satisfactory experimental evidence of the chemical individuality of these substances has as yet been obtained.

Bismuth Suboxide, BiO.—The question as to the existence of an oxide of this composition has given rise to much discussion,[2] but the experimental evidence renders it probable that the suboxide is a definite chemical substance.

The suboxide was first described by Berzelius. It is best obtained by gently heating basic bismuth oxalate, $(BiO)_2C_2O_4$, in absence of air (Tanatar):

$$(BiO)_2C_2O_4 = 2BiO + 2CO_2,$$

or by carefully adding an alkaline solution of stannous hydroxide (1 mol.) to bismuth hydroxide (1 mol.) suspended in dilute potash, washing the suboxide first with dilute potash in absence

[1] Joannis, *Compt. rend.*, 1892, **114**, 585.

[2] Vanino and Treubert, *Ber.*, 1898, **31**, 1113, 2267; 1899, **32**, 1072; where the older literature is quoted. See also Schneider, *J. pr. Chem.*, 1898, [2], **58**, 562; 1899, [2], **60**, 524; Tanatar, *Zeit. anorg. Chem.*, 1901, **27**, 437; Herz and Guttmann, *Zeit. anorg. Chem.*, 1907, **53**, 63; Vanino and Zumbusch, *Arch. Pharm.*, 1910, **248**, 665.

of air until all traces of stannic oxide are removed, then washing with water, and finally drying at 120° in a current of carbon dioxide (Schneider). It is a black powder which is stable in the air and has the specific gravity 7·2, this being considerably less than that of a mixture of bismuth and its oxide having the same percentage composition as the suboxide (8·9). When heated in the air it passes into the trioxide with incandescence, and in absence of air is converted into a mixture of bismuth and bismuth oxide.

The suboxide is converted by hydrochloric acid into bismuth chloride, which dissolves, and insoluble metallic bismuth. The heat evolved in this reaction is considerably less than that produced when a corresponding amount of the trioxide is dissolved, and this affords a further proof of the individuality of the suboxide (Tanatar). It reduces Fehling's solution and potassium permanganate, and is converted by excess of alkaline stannous chloride into metallic bismuth.

Bismuth Trioxide, Bi_2O_3, is found as bismuth ochre in Cornwall, Virginia, Siberia, and Erzgebirge, as a yellow or greenish-grey amorphous mass or as a powder, and it usually contains ferric oxide and other impurities. In order to prepare it artificially, the hydroxide, carbonate, or nitrate is heated. Thus obtained, it is a yellow powder having a specific gravity of 8·2. It fuses at 820°, forming a brown liquid, and when this is allowed to cool the solid which is first formed passes at 704° with evolution of heat into a second modification, which forms a yellow, crystalline mass. When fused in porcelain a third form is produced which crystallises in long, yellow needles of specific gravity 8·55.[1] When a boiling solution of a bismuth salt is precipitated with potash the trioxide is obtained in microscopic needles, and if this be melted with caustic potash the product is found to crystallise in rhombic prisms. When the oxide is prepared by adding potassium cyanide to bismuth nitrate solution, boiling and heating the resulting grey powder in the air, it crystallises in tetrahedra belonging to the regular system. It is therefore isodimorphous with antimony oxide.[2] The oxide prepared by roasting the metal appears to have been employed as a yellow paint in Agricola's times.

Bismuth trioxide is a stronger base than the corresponding oxide of antimony, and forms a well-defined series of salts, which

[1] Gürtler, *Zeit. anorg. Chem.*, 1903, **37**, 222.

[2] Muir and Hutchinson, *Journ. Chem. Soc.*, 1889, **55**, 143.

are characterised by the ease with which they are converted by water into insoluble basic salts.

Bismuth Trihydroxide, $Bi(OH)_3$, is obtained as a white, amorphous powder by precipitating a bismuth salt with cold caustic soda or ammonia. It is soluble in caustic potash in the presence of glycerol,[1] and when precipitated from this solution by acids is free from basic salts, which are always present in the hydroxide prepared by precipitation with alkalis.[2] When dried at 100° it has the composition Bi_2O_3,H_2O or BiO.OH.

Higher Oxides of Bismuth.—When a current of chlorine is passed into a boiling solution of caustic potash containing bismuth hydroxide in suspension a red powder separates out, which contains potassium and yields chlorine on boiling with hydrochloric acid. When this substance is treated with hot concentrated nitric acid, a scarlet-coloured powder remains which has frequently been regarded as bismuthic acid, $HBiO_3$, and from this compounds described as bismuth pentoxide, Bi_2O_5, and potassium bismuthate, $KBiO_3$, have been prepared, both of which are extremely unstable. Under varying conditions the nature of the products obtained in this reaction also varies and substances described as bismuth tetroxide, Bi_2O_4, a brown powder, and the dihydrate of this oxide, $Bi_2O_4,2H_2O$, an orange-yellow powder, have also been prepared by means of it. Similar highly oxidised products are formed by the electrolytic oxidation of the trioxide, and by the action of persulphates, of hydrogen peroxide, and of potassium ferricyanide on the trioxide in the presence of alkali.[3] It has however, been shown by Gutbier and Bünz[4] that none of these reactions leads in any case to a definite homogeneous product. The exact nature of the higher oxidation products of bismuth trioxide, therefore, remains for the present undetermined. In their colour and insolubility in nitric acid the substances obtained exhibit an analogy with lead dioxide, PbO_2.

[1] Löwe, *Zeit. anal. Chem.*, 1883, **22**, 498.

[2] Thibault, *J. Pharm.*, 1900, [6], **12**, 559.

[3] See Deichler, *Zeit. anorg. Chem.*, 1899, **20**, 81, where a critical discussion of the earlier literature will be found. Muir, *Journ. Chem. Soc.*, 1887, **51**, 77; Hollard, *Compt. rend.*, 1903, **136**, 229; Hauser and Vanino, *Zeit. anorg. Chem.*, 1904, **39**, 381; Aloy and Frébault, *Bull. Soc. chim.*, 1906, [3], **35**, 396; Moser, *Zeit. anorg. Chem.*, 1906, **50**, 33.

[4] *Zeit. anorg. Chem.*, 1906, **48**, 162, 294; **49**, 432; **50**, 210; 1907, **52**, 124; *Chem. Centr.*, 1909, i., 732.

Bismuth and the Halogens.

462 *Bismuth Trifluoride*, BiF_3, is obtained as a white powder by dissolving the oxide in hydrofluoric acid and evaporating the solution. An *oxyfluoride*, BiOF, is formed when the acid is completely neutralised by the oxide. The fluoride forms a double salt with ammonium fluoride, BiF_3,NH_4F.[1]

Bismuth Dichloride, $BiCl_2$, is formed when a slow current of chlorine is passed over the fused metal, or when the metal is heated with calomel to 250° or fused with the trichloride. It is a black, crystalline, slightly volatile mass, which when heated decomposes with separation of a portion of the metal and formation of the trichloride. Water decomposes it with formation of metallic bismuth and the oxychloride, BiOCl.

Bismuth Trichloride, $BiCl_3$, was first prepared by Boyle[2] by heating bismuth with corrosive sublimate. It is also formed when the metal is burnt in a stream of chlorine, or when a concentrated solution of the oxide in hydrochloric acid is distilled, the receiver being changed after all the water has come over. Bismuth trichloride is a granular, white mass, which melts at from 225° to 230°, boils at 435° to 441°, and yields a vapour having the normal specific gravity of 11·35 (Jaquelain). Heated in a current of hydrogen it is reduced to dichloride.[3] It forms a syrupy liquid when dissolved in a small quantity of water, though a larger quantity of water decomposes it, with formation of *bismuth oxychloride*, BiOCl, which is thrown down as a pure white powder, insoluble in water, though readily soluble in acids. It separates from a hot acid solution in tetragonal crystals[4] of the sp. gr. 7·717 at 15°, and is decomposed by excess of caustic potash.[5] Heated in the air, bismuth oxychloride loses chlorine and takes up oxygen, but in absence of air it becomes yellow-coloured and fuses without decomposition.

When a solution of the oxide in an excess of hydrochloric acid is evaporated, fine needle-shaped crystals are deposited, having the composition $BiCl_3,2HCl$, whilst at 0° a saturated solution

[1] Helmholt, *Zeit. anorg. Chem.*, 1892, **3**, 115; see also Muir, Hoffmeister and Robbs, *Journ. Chem. Soc.*, 1881, **39**, 33.

[2] *Experiments and Considerations Touching Colours.*

[3] Muir, *Journ. Chem. Soc.*, 1876, i., 144.

[4] de Schulten, *Bull. Soc. chim.*, 1900, [3], **23**, 156.

[5] Herz and Muhs, *Zeit. anorg. Chem.*, 1904, **39**, 115.

of the two deposits crystals of the compound $2BiCl_3,HCl,3H_2O$, which are stable at the ordinary temperature.[1] Bismuth trichloride forms double salts with the chlorides of the alkali metals,[2] and with many organic bases. Ammonia yields three compounds—$BiCl_3,3NH_3$, a very volatile colourless substance; $BiCl_3,2NH_3$, a dirty-grey non-volatile mass; and $2BiCl_3,NH_3$, a red, crystalline body. They combine with hydrochloric acid to form double salts, which are also obtained when ammonium chloride is added to the solution of bismuth in the right proportion and the mixture evaporated.[3] When the dichloride is treated with chlorine a brownish-red powder is obtained of Bi_3Cl_8, which decomposes on heating into chlorine, trichloride, and dichloride.

Bismuth trichloride combines also with nitric oxide[4] to form the yellow compound $2BiCl_3,NO$, and with nitrosyl chloride[5] to form an orange-coloured powder, $BiCl_3,NOCl$.

Bismuth Tribromide, $BiBr_3$.—When bromine vapour is passed over powdered bismuth an energetic reaction takes place and a red liquid volatilises. This cools to a golden-yellow, glistening, deliquescent, crystalline mass, which melts at 210° and boils at 453°. Bismuth tribromide crystallises from ether in prisms, and water decomposes it into the white insoluble *oxybromide*, BiOBr. It forms crystalline double salts with the bromides of the alkali metals, and with ammonia yields compounds similar to those of the chloride.

If the tribromide be fused with bismuth a mass of brown, crystalline needles is obtained, probably consisting of the *dibromide*. This is decomposed by hydrochloric acid with separation of spongy bismuth.

Bismuth Tri-iodide, BiI_3, is obtained by treating the powdered metal with iodine and heating the product; by precipitating a bismuth salt with potassium iodide solution, dissolving in hydriodic acid and reprecipitating with water; or better, by adding bismuth oxide to a solution of iodine in stannous chloride saturated with hydrochloric acid.[6] It sublimes in greyish-black, metallic, glistening, six-sided tablets, which are

[1] Engel, *Compt. rend.*, 1888, **106**, 1797.

[2] See Brigham, *Amer. Chem. J.*, 1892, **14**, 164; Field, *Journ. Chem. Soc.*, 1893, **63**, 546; Aloy and Frébault, *Bull. Soc. chim.*, 1906, [3], **35**, 396.

[3] Dehérain, *Compt. rend.*, 1862, **54**, 924.

[4] Thomas, *Compt. rend.*, 1895, **121**, 128.

[5] Sudborough, *Journ. Chem. Soc.*, 1891, **59**, 662.

[6] Birckenbach, *Ber.*, 1907, **40**, 1404.

not decomposed by cold water, though they are converted by hot water into an insoluble oxyiodide. If a solution of the iodide in hydriodic acid be evaporated, rhombic pyramids of $BiI_3,HI,4H_2O$ are deposited. Bismuth iodide forms a large number of double salts.[1]

Bismuth Oxyiodide, BiOI, is obtained by decomposition of the tri-iodide with boiling water, or by heating the same in the air,[2] as a copper-red, crystalline mass, which can be sublimed when heated in the absence of air, but is gradually converted in presence of air into a crystalline oxide.

Bismuth and the Elements of the Sulphur Group.

463 *Bismuth Subsulphide*, BiS, was first described by Werther[3] and Lagerjhelm[4] as a grey, metallic, lustrous mass of needle-shaped crystals, obtained by fusing bismuth with sulphur and cooling quickly, but this contained free bismuth and the sulphide Bi_2S_3. The existence of the same compound was deduced by Pélabon[5] from the study of the equilibrium curve for bismuth and sulphur and the behaviour of these two elements in the presence of hydrogen, but Aten,[6] employing a similar method of investigation, found no evidence of the formation of the subsulphide in this way.

Bismuth Trisulphide, Bi_2S_3, occurs as bismuthite in rhombic crystals, and also massive with a foliated or fibrous structure, and a specific gravity of 6·4. It is found at Brandy Gill, Carrock Fells in Cumberland, at Redruth and Botallack and other localities in Cornwall, in the Erzgebirge, in Bolivia, and in other places. It is obtained artificially by fusing the metal with an excess of sulphur, or by precipitating a solution of bismuth chloride with sulphuretted hydrogen or sodium thiosulphate. Thus prepared it forms a blackish-brown precipitate easily soluble in nitric acid and in boiling concentrated

[1] Nicklés, *Compt. rend.*, 1860, **50**, 872; *J. Pharm.*, [3], **39**, 116; Linau, *Pogg. Ann.*, 1860, **111**, 240; Wells and Foote, *Amer. J. Sci.*, 1897, **3**, 461; Pfeiffer, *Zeit. anorg. Chem.*, 1902, **31**, 191.

[2] Compare Dubrisay, *Compt. rend.*, 1909, **149**, 451.

[3] *J. pr. Chem.*, 1842, **27**, 65. [4] *Schweiggers Journ.*, 1816, **17**, 416.

[5] *Ann. Chim. Phys.*, 1902, [7], **25**, 365; *J. Chim. phys.*, 1904, **2**, 321; *Compt. rend.*, 1903, **137**, 648, 920.

[6] *Zeit. anorg. Chem.*, 1905, **47**, 386; compare Schneider, *Pogg. Ann.*, 1856, **97**, 480; Herz and Guttmann, *Zeit. anorg. Chem.*, 1907, **53**, 63; 1908, **56**, 422.

hydrochloric acid, but not in alkalis. Its solubility in pure water has been found by the conductivity method to be $0{\cdot}35 \times 10^{-6}$ gram-molecules (0·2 mgm.) per litre. When it is heated to 200° in a solution of an alkali it becomes crystalline, assuming the form of bismuthite, and when heated in the electric furnace yields metallic bismuth.[1]

The amorphous sulphide dissolves in potassium sulphide solution and very sparingly in sodium sulphide solution,[2] and forms salts of the formulæ Bi_2S_3,K_2S and Bi_2S_3,Na_2S when it is fused with sulphur and an alkali carbonate.[3]

Bismuth Oxysulphides.—The compound Bi_4O_3S occurs as karelilinite in a crystalline mass having a strongly metallic lustre found at the Savodinck Mine in the Altai. If a mixture of 40 parts of sulphur and 142 parts of bismuth trioxide are heated to dark redness a grey, crystalline mass of $Bi_6O_3S_4$ is formed.

Bismuth Chlorosulphide, BiSCl, is obtained by fusing together in the air 1 part of sulphur and 8 parts of ammonium bismuth chloride, or by heating the latter compound in a current of sulphuretted hydrogen (Schneider), and is formed also when the chloride is heated in dry sulphuretted hydrogen or the sulphide in dry chlorine. It is a reddish-brown solid and is not decomposed by water. The corresponding *sulphobromide* is obtained in a similar manner, whereas the *sulphiodide* can be prepared only by heating bismuth iodide with the trisulphide. All three compounds are decomposed by sulphuretted hydrogen at a bright red heat.[4]

Bismuth Trisulphate, $Bi_2(SO_4)_3$, is obtained as an amorphous, white mass by dissolving the metal or the sulphide in concentrated sulphuric acid and evaporating. This salt is decomposed by water with formation of the basic salt, $Bi_2O_3,SO_3,2H_2O$. When this is heated it loses water, and on cooling a yellow mass, consisting of Bi_2O_3,SO_3, is obtained. This salt is also obtained by heating the other sulphates. Another of these basic salts has the composition $Bi_2O_3,2SO_3,3H_2O$, and is obtained in small needles by acting upon the nitrate with sulphuric acid. Several other basic salts have also been described.[5] Concentrated

[1] Mourlot, *Compt. rend.*, 1897, **124**, 768.

[2] Ditte, *Compt. rend.*, 1895, **120**, 186. See also *J. Amer. Chem. Soc.*, 1896, **18**, 683, 1091.

[3] Schneider, *Pogg. Ann.*, 1869, **136**, 460.

[4] Muir and Eagles, *Journ. Chem. Soc.*, 1895, **67**, 90.

[5] See Allan, *Amer. Chem. J.*, 1902, **27**, 284.

sulphuric acid yields the acid salt, $Bi_2O_3,4SO_3$, several hydrates of which have been obtained.[1]

Bismuth Thiosulphate.—Complex thiosulphates are obtained by the addition of the alkali thiosulphates to bismuth chloride solution. The *potassium* salt, $K_3Bi(S_2O_3)_3,\frac{1}{2}H_2O$, is sparingly soluble in water, and the solution rapidly decomposes, bismuth sulphide being deposited. This solution does not react with iodine.[2]

464 *Bismuth Triselenide*, Bi_2Se_3, is obtained by fusing the elements together as a metallic, lustrous, brittle, crystalline mass, having a specific gravity of 6·82, which is attacked only by nitric acid and aqua regia.

Bismuth Tritelluride, Bi_2Te_3, occurs as the mineral tetradymite, in which some of the tellurium is replaced by sulphur. It forms pale metallic steel-grey rhombohedra, or foliated or granular masses having a specific gravity of 7·2 to 7·9. Groth [3] considers this mineral to be an isomorphous mixture of the elements, as it is not isomorphous with bismuthite, Bi_2S_3, and as bismuth and tellurium can be fused together in all proportions.

Several other bismuth tellurides of varying composition have been described, some of which occur as minerals. According to Mönkemeyer [4] only one stable compound of these two elements exists; this has the formula Bi_2Te_3 and melts at 573°.

Bismuth and the Elements of the Nitrogen Group.

465 *Bismuth Nitride*, BiN, is formed as a brown precipitate when bismuth iodide dissolved in liquid ammonia is added to a solution of potassamide in the same solvent.[5]

Bismuth Trinitrate, $Bi(NO_3)_3,5H_2O$, is obtained in large transparent, triclinic prisms by dissolving the metal in nitric acid and evaporating the solution, which corrodes paper, and, must, therefore, be filtered through asbestos or pounded glass. The crystals, which are deliquescent, are decomposed on heat-

[1] Adie, *Proc. Chem. Soc.*, 1899, **15**, 226.

[2] Carnot, *Compt. rend.*, 1876, **83**, 338; Hauser, *Zeit. anorg. Chem.*, 1903, **35**, 1.

[3] *Tabell. Uebersicht d. Mineralien*, p. 12 (Braunschweig, 1882, Vieweg).

[4] *Zeit. anorg. Chem.*, 1905, **46**, 415; see also Gutbier, *ibid.*, 1902, **31**, 331.

[5] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

ing, first losing their water, and then leaving a residue, first of basic salt, and lastly of the trioxide. Hydrates with 2 and $1\frac{1}{2}H_2O$ also exist.[1]

Bismuth nitrate is isomorphous with the nitrates of yttrium, lanthanum, and others of the rare earth metals,[2] and forms double salts which are isomorphous with the corresponding salts of the rare earths and have been utilised in the fractional crystallisation of mixtures of these (p. 778).[3]

When hydrated bismuth nitrate is ground with mannitol and water added, a clear solution is formed which is not precipitated on dilution and serves as a means of preparing many insoluble bismuth salts by double decomposition.[4]

Basic Bismuth Nitrate, $Bi(OH)_2NO_3$.—Libavius was aware that the solution of bismuth in nitric acid is precipitated by water, and Lemery, who describes the preparation of this compound, states that water containing common salt should be employed for this precipitation, pure water precipitating it, but much more slowly; and he adds that the product obtained weighs more than the metal employed. The reason of this, he explains, is that a certain quantity of spirit of nitre remains behind, even if the precipitate be well washed. Boyle states that the solution of bismuth in aqua-fortis is almost completely precipitated by common water. In spite of this, many chemists, looking at the analogy between lead and bismuth, believed that salt water was necessary for the precipitation; indeed, the substance was for some time termed horn-bismuth. This error was definitely rectified by Pott, in 1739.

Basic nitrate of bismuth, formerly termed *magistery of bismuth*, is used as an important medicine, and many different receipts are given for its preparation. According to the method formerly prescribed in the British Pharmacopœia (1874), *bismuth subnitras* is best obtained by dissolving 2 parts by weight of bismuth in a mixture of 4 parts of nitric acid of specific gravity 1·42 with 3 parts of water. The clear liquid is poured off from any insoluble matter and evaporated to the point at which it occupies two volumes, and this is then poured into

[1] van Bemmelen and Rutten, *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 196.

[2] Bodman, *Ber.*, 1898, **31**, 1237; *Zeit. anorg. Chem.*, 1901, **27**, 254; *Zeit. Kryst. Min.*, 1902, **36**, 192.

[3] Urbain, *Compt. rend.*, 1903, **137**, 568; *J. Chim. phys.*, 1906, **4**, 105.

[4] Vanino and Hauser, *Zeit. anorg. Chem.*, 1901, **28**, 210; *J. pr. Chem.*, 1906, [2], **74**, 142.

80 parts of distilled water. The clear liquid is then decanted and the precipitate well stirred up with 80 parts of water, collected on a filter, and dried at a temperature not higher than 55°. The German and French pharmacopœias recommended somewhat similar processes. In all these methods a considerable quantity of bismuth remains in solution, and this may be obtained, as the hydroxide, by precipitating with ammonia. The bismuth is completely precipitated when 50,000 parts of water are present to one of the nitrate.[1]

Basic bismuth nitrate is a crystalline powder which reddens moistened litmus paper. Its composition varies somewhat according to the quantity of water used in the preparation, and a large number of basic salts have been described, the conditions of formation and existence of which have been investigated by van Bemmelen and Rutten,[2] by Allan,[3] and by de Schulten.[4] When washed for a long time it becomes more basic, until at last the hydroxide is left.

Basic bismuth nitrate is largely used as a medicine in cases of chronic diarrhœa and cholera. It is, moreover, used in considerable quantities as a cosmetic; and this use is due to Lemery, who recommends it for softening the skin. When used for this purpose it was first termed *blanc d'Espagne*, which name, however, was used to designate many other white pigments. Another name for this cosmetic is *blanc de fard*.

The basic nitrate, as well as the oxide, is also used for giving a colourless, iridescent glaze to porcelain. This is obtained by rubbing up basic nitrate with resin and gently heating the mixture with lavender oil, and can be coloured by the addition of oxides, such as oxide of chromium, which gives to it a sulphur or lemon-yellow colour. With addition of 5 per cent. of gold to the oxide of bismuth, a splendid copper-red colour with a reflected golden lustre is obtained. When a smaller quantity of this same substance is employed the glaze assumes a violet or pure blue colour, whilst with another treatment a rose-red tint is obtained. These glazes are also used in glass-staining.

466 *Bismuth Orthophosphate*, $BiPO_4$, is precipitated when solutions of bismuth nitrate and phosphoric acid are brought together

[1] Antony and Gigli, *Gazz.*, 1898, **28**, i., 245.
[2] *Proc. K. Akad. Wetensch. Amsterdam*, 1900, **3**, 196.
[3] *Amer. Chem. J.*, 1901, **25**, 307.
[4] *Bull. Soc. chim.*, 1903, [3], **29**, 720.

in presence of nitric acid. When slowly precipitated by water from acid solution it forms microscopic crystals of sp. gr. 6·323 at 15° (de Schulten). In the same way an insoluble *pyrophosphate*, $Bi_4(P_2O_7)_3$, is prepared with pyrophosphoric acid. When the oxide and phosphorus pentoxide are fused together, a clear glass is obtained, which on slow cooling becomes crystalline, and probably consists of the tetrametaphosphate.

Bismuth Arsenate, $Bi_4(As_2O_7)_3$, is a white precipitate insoluble in water and nitric acid, but soluble in hydrochloric acid. The *ortho-arsenate*, $BiAsO_4$, forms monoclinic prisms of sp. gr. 7·142 at 15° (de Schulten).

Phosphorus and *arsenic* do not readily combine with bismuth. The first of these forms a compound with molten bismuth, and if a current of phosphine be passed through a solution of bismuth, a black phosphide is precipitated, which, however, decomposes in absence of air into its elements. An alloy of bismuth and arsenic gives up the whole of the latter when heated. Arsine produces a black precipitate in bismuth solutions which behaves in a precisely similar way.

Bismuth and the Elements of the Carbon Group.

467 *Basic Bismuth Carbonate*, $2(BiO)_2CO_3,H_2O$, is obtained as a white powder when ammonium carbonate is poured into a solution of bismuth nitrate and the precipitate dried at a gentle heat. It is employed as a medicine. At 100° it loses water, and when more strongly heated is readily converted into the trioxide.

The mineral bismuthite is another basic carbonate,

$$3(BiO)_2CO_3,2Bi(OH)_3,3H_2O.$$

This is found at Schneeberg, at Chesterfield, South Carolina, and at other places, together with bismuthores. It is a white or siskin-green earthy mass, and sometimes occurs in acicular pseudomorphous crystals.

Bismuth Silicate, $Bi_4(SiO_4)_3$, is found as eulytite in small, glistening yellow or brown regular tetrahedra and occurs in the Erzgebirge together with phosphates of iron and manganese.

Detection and Estimation of Bismuth.

468 When a bismuth compound is heated in the upper reducing flame of the Bunsen burner on an asbestos thread, a cold porcelain dish, held above it, receives a brown or black deposit

of metallic bismuth, which is only slowly dissolved by cold dilute nitric acid. A brittle metallic bead is obtained when the compound is heated on the carbonised match, and this dissolves in nitric acid, yielding a brown precipitate of bismuth with excess of stannous chloride and caustic soda. A characteristic reaction of the bismuth salts is the precipitation of the blackish-brown sulphide with sulphuretted hydrogen, insoluble in ammonium sulphide, and easily soluble in nitric acid. In addition to this, water produces, in solutions which are not too strongly acid, a white precipitate of an insoluble basic salt, and ammonia throws down a white precipitate of the hydroxide insoluble in excess. These reactions serve to separate bismuth from other metals, as well as to detect its presence. If other metals precipitable by sulphuretted hydrogen are present, the washed precipitate is first digested with ammonium sulphide, in order to separate arsenic, antimony, and tin. The precipitate is then well washed, dissolved in nitric acid, and dilute sulphuric acid added to the filtrate to separate lead; the precipitate is filtered off, and an excess of ammonia added which throws down the bismuth as the hydroxide, whilst any copper or cadmium present remains in solution. The precipitate is dissolved in a small quantity of hydrochloric acid, the liquid concentrated by evaporation, and added to a large quantity of water, when the insoluble oxychloride is precipitated. Care, however, must be taken that the whole of the antimony is previously removed by a long digestion of the sulphides with ammonium sulphide, and the residue well washed with water, for otherwise an insoluble oxychloride of antimony may be precipitated, and this may be mistaken for bismuth.

Bismuth can be estimated in several ways. If the solution contains the nitrate only, it may be precipitated with ammonium carbonate, heated for some time almost to boiling, filtered, the precipitate dried and converted by ignition into the trioxide, which is weighed. If other acids are present, the bismuth is precipitated by sulphuretted hydrogen, the washed precipitate dissolved in nitric acid and treated as above; or it may be dried, any excess of sulphur got rid of by carbon disulphide, and the residual pure sulphide dried at 100° and weighed. The phosphate may also be precipitated in the presence of phosphoric acid or dilute nitric acid, ignited, and weighed.[1] If the solution of the nitrate contains only a small quantity of

[1] *Ber.*, 1905, **38**, 3862, 3943.

free acid it may be precipitated with potassium dichromate, or with arsenic acid, and the precipitate dried and weighed. Bismuth may also be estimated as the metal by reduction with potassium cyanide. The metallic mass is well washed with water and alcohol, and weighed after drying. Bismuth may also be separated electrolytically from an acid solution of the nitrate in the presence of alcohol, glycerol, or acid potassium sulphate.[1]

The Atomic Weight of bismuth has been determined by several chemists, but without very concordant results. In 1851 Schneider,[2] by converting the metal into the oxide, obtained the number 208·05, and this was confirmed in 1883 by Löwe,[3] who used the same method and obtained the number 207·8, and by Marignac,[4] who, in 1883, found the atomic weight to be 208·16 by converting the oxide into the sulphate. Dumas,[5] on the other hand, in 1859, by the analysis of the chloride, obtained the number 210·7, which is certainly too high. In 1890 Classen[6] made a series of nine concordant experiments in which carefully purified bismuth was converted into the oxide and found the number 208·9. Schneider, in 1894,[7] repeated his experiments and again obtained the number 208·05. The older determinations have been confirmed by the results obtained by Gutbier[8] and his co-workers, who obtained the values 208·02—208·15 by converting the metal into oxide, reducing the oxide to metal, converting the metal into sulphate, and determining the ratio $BiBr_3 : AgBr$. The value 208·0 is therefore (1913) adopted.

[1] *Compt. rend.*, 1900, **131**, 179; *Zeit. anorg. Chem.*, 1901, **27**, 1; *J. Amer. Chem. Soc.*, 1903, **25**, 83.

[2] *Pogg. Ann.*, 1851, **82**, 303. [3] *Zeit. anal. Chem.*, 1883, **22**, 498.

[4] *Zeit. anal. Chem.*, 1884, **23**, 120.

[5] *Ann. Chim. Phys.*, 1859, [3], **55**, 177. [6] *Ber.*, 1890, **23**, 938.

[7] *J. pr. Chem.*, 1894, **56**, 461.

[8] *Zeit. Elektrochem.*, 1905, **11**, 831; *J. pr. Chem.*, 1908, ii., **77**, 457; ii. **78**, 409, 421. See also the Dissertations (Erlangen) of Birckenbach, 1905; Mehler, 1905; and Janssen, 1906.

GROUP VI.

Sub-Group (*a*). Oxygen and the Sulphur Group.

Oxygen.
Sulphur.
Selenium.
Tellurium.

Sub-Group (*b*). The Chromium Group.

Chromium.
Molybdenum.
Tungsten.
Uranium.

469 In this group, as in Groups I, II, and III, the elements may be divided into two well-defined sub-groups, as shown in the above list, the sub-group (*a*) consisting of non-metallic elements, while those in the sub-group (*b*) are metals. In the strict periodic classification oxygen falls in the even series, and therefore belongs to the chromium sub-group, but as in the case of glucinum in Group II, it is much more nearly allied to the members of the odd series.

Oxygen is gaseous at the ordinary temperature, whilst sulphur, selenium, and tellurium are solids, the melting and boiling points of which rise with increasing atomic weight. The elements of the chromium group are fusible only at very high temperatures, and are reduced from their oxides only with great difficulty.

All the metals unite with the elements of the oxygen group to form oxides, sulphides, selenides, and tellurides; and the different series of compounds thus formed present strong analogies among themselves, as has already been seen in the description of the compounds of the metals of the previous groups. The analogy which exists between the "oxy-salts"

obtained by the union of a basic and acidic oxide, and the "thio-salts" formed in a similar manner from the acidic and basic sulphides, has also been frequently alluded to.

The most characteristic compounds formed by these elements (with, of course, the exception of oxygen) are the trioxides and their numerous derivatives. All of these behave as acid-forming oxides, and give rise to well-defined series of compounds having the general formula $M^{I}_{2}R^{VI}O_4$, in which M^{I} represents hydrogen, or a monovalent metal, and R^{VI} an element of the group under consideration. These possess strongly marked analogies with each other, and the salts of the same metal are as a rule isomorphous. These oxides also form salts containing from two to eight equivalents of the acidic oxide to one of basic oxide, such as the disulphates, $M^{I}_{2}O,2SO_3$, and dichromates, $M^{I}_{2}O,2CrO_3$, the trichromates, $M^{I}_{2}O,3CrO_3$, the octotungstates, $M^{I}_{2}O,8WO_3$, &c.

The constitution of the normal acids corresponding to the trioxides is represented by the formula $O_2R^{VI}\langle^{OH}_{OH}$, and the hydroxyl groups in these acids may be replaced by negative radicals such as the halogens. The compounds thus formed from the elements of lower atomic weight, such as sulphur and chromium, are acidic chlorides, and are at once decomposed by water with formation of the acid; but as the atomic weight of the element increases, the basicity of the radical $R^{VI}O_2$ also increases, and the compounds become more stable, until in the case of uranium, the compounds formed by negative radicals with the group UO_2 constitute the most stable series of salts of that metal.

The elements of this group also form other oxides containing a less amount of oxygen than the trioxide; in the case of sulphur, selenium, and tellurium, these oxides (RO_2) are acidic or neutral, whilst with the metals of the chromium group (RO, R_2O_3 and RO_2) they are usually basic, and give rise to series of salts which often have strong reducing properties, owing to their tendency to unite with oxygen, forming derivatives of the trioxide.

The elements of sub-group (*a*) combine with hydrogen and the alkyl radicals forming volatile compounds, but no similar derivatives have been obtained from the elements of sub-group (*b*).

Oxygen is divalent in almost all of its compounds, but pos-

sibly sometimes acts as a tetrad. The remaining elements are, as stated above, hexavalent in their most characteristic oxygen compounds, but the valency in their other compounds, especially with the halogens, varies very considerably; the elements sulphur, selenium, and tellurium are always divalent towards hydrogen and the alkyl radicals, and usually either di-, tetra-, or hexa-valent in their other compounds, but no such regularity is observed in sub-group (*b*).

The compounds of oxygen, sulphur, selenium, and tellurium have already been described in Vol. I.

CHROMIUM. Cr = 52·0.

470 In 1762 Lehmann, in a letter to Buffon, "de nova mineræ plumbi specie crystalline rubra," described a new mineral from Siberia, now termed crocoisite or lead chromate. Vauquelin and Macquart investigated the composition of this mineral in 1789, and came to the conclusion that it contained lead, iron, alumina, and a large quantity of oxygen. However, when the former chemist re-investigated the subject in 1797, he found that the lead present was combined with a peculiar acid, which he recognised as the oxide of a new metal. To this the name of *chromium* was given, because its compounds are usually coloured (from *χρῶμα*, colour). The discovery of this new metal in crocoisite was also made simultaneously and independently by Klaproth.

Chromium is not a very common substance, and does not occur in the free state. It is found in several other minerals besides crocoisite or lead chromate, $PbCrO_4$, especially as chrome iron stone or chromite, FeO,Cr_2O_3, a mineral which is the chief ore of chromium and is the one usually employed for the manufacture of the chromium compounds. Chromitite, Fe_2O_3,Cr_2O_3, occurs as minute shining crystals in the sand of some of the streams descending from the Kopanik Mountains, Servia.[1] Chromium also forms the colouring matter of several minerals; thus the green colour of emerald, as was shown by Vauquelin, is due to chromium; whilst serpentine, pennine, chromic mica or fuchsite, possibly sapphire,[2] and other minerals owe their colour to the same metal.

[1] Jovitschitsch, *Monatsh.*, 1909, **30**, 39.
[2] Duboin, *Ber.*, 1898, **31**, 1977.

Metallic chromium is obtained by the reduction of the oxide or chloride; thus Deville obtained it by strongly heating the oxide with sugar charcoal in a lime crucible,[1] and Wöhler by heating chromic chloride with zinc under a layer of sodium chloride, and treating the alloy of zinc and chromium thus obtained with nitric acid;[2] it then forms a grey powder consisting of minute octahedra.[3] Jäger and Krüss obtained the pure metal by this process in tin-white rhombohedra.[4] Magnesium and sodium have also been employed in place of metallic zinc, the first of these being specially suitable for a laboratory preparation. Another method of preparation is that of Moissan,[5] which consists in heating a mixture of chromium sesquioxide and carbon in the electric furnace; the first product contains large quantities of carbon, which is removed by first heating strongly with lime, when the greater part of the carbon is converted into calcium carbide, and then eliminating the remainder by fusing the purified product in a crucible brasqued with the double oxide of calcium and chromium.

Metallic chromium is easily prepared from chromic oxide by the "thermite" process (p. 716), which consists in mixing finely-divided aluminium with chromic oxide in equivalent proportions and igniting the mixture.[6] The following reaction takes place:

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3.$$

When once started the reduction proceeds rapidly with great evolution of heat, and produces a fused mass of metallic chromium of considerable purity. This is shown by the following analysis:[7]

Cr 99·55, Fe 0·14, Si 0·31.

Large quantities of chromium are now used in the form of ferro-chrome, manufactured by the reduction of chromite in the electric furnace or by means of aluminium; these ferro-chromes generally contain between 60 and 70 per cent. of chromium. Chromium has also been prepared by the electrolysis

[1] *Compt. rend.*, 1857, **44**, 673.
[2] *Annalen*, 1859, **111**, 230.
[3] Prinz, *Compt. rend.*, 1893, **116**, 392.
[4] *Ber.*, 1889, **22**, 2052.
[5] *Compt. rend.*, 1893, **116**, 349; 1894, **119**, 185; *Ann. Chim. Phys.*, 1896, [7], **8**, 559.
[6] *J. Soc. Chem. Ind.*, 1898, **17**, 543.
[7] *J. Iron Steel Inst.*, 1902, **1**, 185.

of a warm solution of chromic chloride or of a cold solution acidified with hydrochloric acid, and is thus obtained as a bright silver-white deposit.[1] It can also be deposited from the violet solutions of chrome alum, but not from the green solutions.

Pure chromium is somewhat harder than glass, and has a melting point considerably higher than that of platinum, whilst if it contains 1·5—3 per cent. of carbon it melts at a lower temperature, but can be cut only by the diamond. It may be distilled in the electric furnace.[2] The polished metal resembles iron, but is brighter and has a somewhat whiter colour: it has a specific gravity of 6·92 at 20°, a specific heat of 0·1216, and burns when heated in the oxy-hydrogen flame more brilliantly than iron. It is attacked slowly in the cold and rapidly on heating by dilute hydrochloric acid, and also dissolves slowly in dilute sulphuric and nitric acids. With concentrated sulphuric acid it evolves sulphur dioxide, with formation of a deep-coloured solution, but it is unaffected by hot concentrated nitric acid. Chromium, like iron, has been found to exist in a "passive" state.[3]

471 *Chromium Amalgams.*—When a strong hydrochloric acid solution of chromic chloride is electrolysed with a powerful current, using a mercury cathode and a platinum anode, a solid chromium amalgam is obtained, having the composition Hg_3Cr. Under a pressure of 200 kilos. to the square cm. this loses mercury, yielding an amalgam of the composition HgCr. When either of these amalgams is heated in a vacuum at 300°, the whole of the mercury is driven off, leaving the chromium as a powder, which is pyrophoric at the ordinary temperature, and also combines with nitrogen on heating.[4]

[1] Cowper-Coles, *Chem. News*, 1900, **81**, 16; Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 617; Carveth and Molt, *J. Physical Chem.*, 1905, **9**, 231, 353: *Zeit. Elektrochem.*, 1906, **12**, 329.

[2] Moissan, *Compt. rend.*, 1906, **142**, 425.

[3] Hittorf, *Zeit. physikal. Chem.*, 1898, **25**, 729; 1899, **30**, 481; Ostwald, *Zeit. physikal. Chem.*, 1900, **35**, 33, 204; Morgan and Duff, *J. Amer. Chem. Soc.*, 1900, **22**, 331; Brauer, *Zeit. physikal. Chem.*, 1901, **38**, 441; Döring, *J. pr. Chem.*, 1902, [2], **66**, 65; Bernoulli, *Physikal. Zeit.*, 1904, **5**, 632.

[4] Férée, *Compt. rend.*, 1895, **121**, 822.

COMPOUNDS OF CHROMIUM.

Chromium and Oxygen.

472 Chromium combines with oxygen to form the well-defined oxides, chromium sesquioxide, Cr_2O_3, and chromium trioxide, CrO_3. The former is a basic oxide, corresponding to the chief series of chromium salts, in which the metal is trivalent; whilst the latter is an acidic oxide, which combines with water to form chromic acid, H_2CrO_4, the salts of which resemble the corresponding sulphates, selenates, and tellurates, and are frequently isomorphous with them.

In addition to these, chromium monoxide, CrO, and the corresponding hydroxide have been prepared, and the latter yields with acids the *chromous* salts, in which the metal is divalent. A number of other oxides have been described which may be regarded as formed by the combination of one or other of the basic oxides with the acidic trioxide; the best defined of these is that frequently termed chromium dioxide, which has really the constitution $Cr_2O_3.CrO_3 = 3CrO_2$, and will be described with the other chromates.

Chromium Monoxide, CrO.—An oxide of this composition is obtained as a black powder by the oxidation of chromium amalgam by exposure to air. When heated in air or when struck with a hammer it inflames and burns to the sesquioxide. It is insoluble in nitric acid, but dissolves in hydrochloric acid with liberation of hydrogen and formation of chromous and chromic chlorides.[1]

Chromous Hydroxide, $Cr(OH)_2$, is formed by the action of aqueous potash, freed from air, on chromous chloride solution, as a brownish-yellow precipitate, which is readily oxidised with evolution of hydrogen, and on drying in absence of air has a dark brown colour. On ignition it yields water, hydrogen, and chromium sesquioxide:

$$2Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

Chromium Sesquioxide, or *Chromic Oxide*, Cr_2O_3, occurs in the hydrated form as chrome ochre, and is obtained artificially as a dull green amorphous powder by igniting the hydroxide, or by heating a mixture of potassium dichromate with sulphur or

[1] Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 619.

ammonium chloride, and lixiviating the residue. The colour of the oxide prepared by gently igniting mercurous chromate, Hg_2CrO_4, in a covered crucible is a very fine green. It melts at the temperature of the oxy-hydrogen blowpipe, solidifying to a crystalline, almost black mass. Chromic oxide is also obtained in the crystalline state by fusing the amorphous substance with calcium carbonate and boron trioxide, or by ignition in a stream of oxygen. Wöhler's[1] method of preparing crystalline chromic oxide consists in passing the vapour of chromyl dichloride, CrO_2Cl_2, through a red-hot tube, when chromic oxide is deposited in dark-green, lustrous, very hard, hexagonal crystals, which have a specific gravity of 5·21. Another method consists in heating potassium dichromate either alone or, better, mixed with common salt; the ignited mass is dissolved in water, when chromic oxide remains in bright iridescent spangles, which have a specific gravity of 5·01.[2]

The strongly ignited oxide is almost insoluble in acids, and in order to bring it into solution it must either be heated for a long time with strong sulphuric acid, or fused with acid potassium sulphate. Chromic oxide is used in the preparation of coloured glass, enamels, and porcelain, imparting to them a fine green tint. It is also used in ordinary painting, forming one of the most permanent greens, known as chrome-green.

Chromic Hydroxides.—Several modifications of chromic hydroxide are known; the first, which reacts directly with three equivalents of acid forming the normal chromic salts, is obtained by the action of alkalis on cold solutions of violet chromic salts, and has probably the constitution $Cr(OH)_3$. It is best prepared by adding ammonia to a solution of a violet chromic salt free from alkali, and forms a pale blue precipitate, which, after drying over sulphuric acid, has the composition $Cr(OH)_3,2H_2O$. When heated in a current of hydrogen at 200° it yields the hydroxide, CrO(OH), which occurs mixed with clay as chrome ochre or wolchonskoïte; at a red heat this commences to glow strongly and passes into chromic oxide. A hydroxide of this composition, or Cr_2O_3,H_2O, has also been obtained as a brown substance by the electrolysis of neutral solutions of chromic chloride.[3] Another hydroxide, which has

[1] *Annalen*, 1846, **60**, 203.

[2] Schröder, *Pogg. Ann.*, 1859, **106**, 226; **107**, 113; see also Ditte, *Compt. rend.*, 1902, **134**, 336.

[3] Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 620.

probably the constitution $Cr_2O(OH)_4$, is obtained by dissolving the first-named hydroxide in caustic soda and reprecipitating with hydrochloric acid, and is also formed by the action of alkalis on the green chromic salts of oxy-acids (p. 1046); when treated with acids it reacts with only two equivalents of the latter, yielding the above green salts, which, however, on standing with acid gradually combine with it, forming the normal violet salts. Another hydroxide which also reacts with only two equivalents of acid is formed, according to Recoura, by the action of alkalis on the chromic oxychloride obtained by oxidation of chromous chloride solution. It differs from the foregoing in the amount of heat evolved by the action of two equivalents of acid.[1]

Guignet's Green is obtained by fusing together potassium dichromate and crystallised boric acid in equal molecular proportions and lixiviating the fused mass with water. The residue after grinding is a fine green powder, and is largely used as a pigment. It is usually described as having the composition $Cr_2O(OH)_4$, but it always contains boric acid, and may possibly have the composition $3Cr_2O_3,B_2O_3,4H_2O$.

Colloidal Chromic Hydroxide.—Freshly precipitated and washed chromic hydroxide dissolves in chromic chloride, and on dialysing this solution Graham obtained a liquid containing 33 molecules of Cr_2O_3 to one of HCl. The dark green solution does not undergo change on boiling or dilution, but at once coagulates on addition of the smallest quantity of a salt.[2] The precipitated colloid has no constant composition between 15° and 280°.[3]

Chromites.—Like alumina, chromic oxide acts as an acidic oxide towards strong bases, yielding salts termed the chromites. Thus a green compound of chromic oxide with an alkali is thrown down on the addition of potash or soda to a solution of a chromic salt, and the alkali cannot be removed even by boiling water. This precipitate is, however, easily soluble in an excess of the precipitant, but can be again thrown down either by partial neutralisation with acids or by boiling the solution. When caustic soda is added to a solution of a chromic salt and a salt of magnesium, a precipitate is obtained of a compound of magnesia and chromic oxide which does not dissolve in an excess of alkali.

[1] *Ann. Chim. Phys.*, 1887, [6], **10**, 60.
[2] Graham, *Phil. Trans.*, 1861, **151**, 183.
[3] van Bemmelen, *Rec. trav. chim.*, 1887, **7**, 114.

The chromites may be obtained also by the action of boiling aqueous alkalis on the corresponding sulphochromites (p. 1048).

Zinc Chromite, $ZnCr_2O_4$, is obtained by fusing the two oxides with boron trioxide at a white heat, when blackish-green octahedra having a specific gravity of 5·309 are obtained.

Manganese Chromite, $MnCr_2O_4$, is obtained in a similar way, and forms very hard iron-grey octahedra, which have a specific gravity of 4·87.

Ferrous Chromite, $FeCr_2O_4$.—This occurs in nature as chromite or chrome iron ore. It is rarely found crystallised in regular octahedra, generally occurring massive, with a granular crystalline fracture. Alumina and magnesia occur frequently as isomorphous constituents, and in some cases chromite contains more iron than corresponds to the above formula, the composition approximating to $Fe_2Cr_2O_5$,$Fe_3Cr_4O_9$.[1] Chrome iron ore is found in the Shetland Islands, Norway, the United States, Hungary, Greece, Asia Minor, in the Urals, and in New Caledonia.

Chromium Trioxide, Chromic Acid, and the Chromates.

473 When chromic oxide is heated to redness with an alkali in presence of air or with addition of an oxidising agent such as nitre, potassium chlorate, &c., a yellow soluble mass is obtained, consisting of an alkali chromate. The chromates are also formed when an alkaline solution of chromic oxide is treated with lead peroxide, potassium permanganate, chlorine, bromine, hypochlorites, or other oxidising agents:

$$Cr_2O_3 + 10KOH + 3Br_2 = 2K_2CrO_4 + 6KBr + 5H_2O.$$

The chromates usually possess a yellow, yellowish-red, or red colour. Besides the normal salts we are acquainted with basic salts, but not with any acid salts. The salts frequently termed acid salts are dichromates corresponding to the disulphates, and are salts of dichromic acid, $H_2Cr_2O_7$ (p. 1027). Of these the most important is common red potassium dichromate, $K_2Cr_2O_7 = K_2CrO_4,CrO_3$. We are acquainted also with trichromates and other polychromates.

Chromium Trioxide or *Chromic Anhydride*, CrO_3.—This compound is formed by the action of strong sulphuric acid on solutions of the chromates. According to Zettnow[2] the best yield is ob-

[1] Christomanos, *Ber.*, 1877, **10**, 343.

[2] *Pogg. Ann.*, 1871, **143**, 471.

tained when 300 grams of potassium dichromate are mixed with 500 c.c. of water, 420 c.c. of concentrated sulphuric acid added, and the mixture allowed to stand for twelve hours in order that the acid potassium sulphate may crystallise out. The mother-liquor is then heated to 80° or 90°, and 150 c.c. of sulphuric acid added, together with enough water to dissolve the crystals of trioxide which at first separate out. After standing for twelve hours the liquid is poured off from the crystals which have separated, and a second and a third crop may be obtained by concentration. The liquid is drained off from the crystals, and these are then washed on a pumice-stone or asbestos filter by the aid of a filter pump with pure nitric acid, having a specific gravity of 1·46, the adhering nitric acid being removed by passing a current of dry air over the crystals heated in a tube at 60°–80°.[1]

Chromium trioxide may also be obtained by the action of an excess of nitric acid of sp. gr. 1·38 on barium chromate, the barium nitrate being separated by crystallisation.[2]

Chromium trioxide exists either as a red woolly mass or as long, scarlet, rhombic prisms with a strong lustre; it has a specific gravity of 2·78, and melts at 193° to a dark red liquid, which solidifies to a reddish-black, crystalline mass, having a metallic appearance. At 250° it is resolved into oxygen and the sesqui-oxide.

Chromium trioxide is easily converted into chromic oxide by reducing agents, such as sulphur dioxide, hydrogen sulphide, stannous chloride, arsenious oxide, ferrous salts, zinc, &c., and many organic compounds also act in the same way. Thus if strong alcohol be dropped on to the dry trioxide reduction takes place with incandescence, and if the trioxide be previously mixed with a little powdered camphor, the chromic oxide formed assumes the appearance of a green mossy vegetation. Paper, sugar, oxalic acid, &c., also reduce the solution of the trioxide, especially on warming. When the trioxide is heated with hydrochloric acid, chlorine is liberated, and when heated with sulphuric acid it decomposes with evolution of oxygen. The aqueous solution of chromium trioxide as well as its solution in glacial acetic acid is often used in organic chemistry as an oxidising agent. Still more commonly a mixture of potassium dichromate and dilute sulphuric acid is employed for this pur-

[1] Bunsen, *Annalen*, 1868, **148**, 290.
[2] Duvillier, *Compt. rend.*, 1867, **65**, 711.

pose, in which case chrome alum is obtained as a by-product. Chromium trioxide dissolves without alteration in cold dilute alcohol and pure ether, and it is soluble also in concentrated sulphuric acid, but not in an acid containing from 16 to 17 per cent. of water. It deliquesces on exposure to air, forming a brown solution which on dilution with water becomes of a yellowish-red colour. This dyes the skin, as well as silk and wool, a yellow colour, and possesses an acid and astringent taste.

Chromic Acid, H_2CrO_4, is obtained by warming the trioxide for some time with a quantity of water insufficient for its complete solution, and decanting the clear liquid. The acid separates out on cooling in rose-red crystals which are stable over sulphuric acid but readily yield the trioxide and water on warming.[1] From the high conductivity of the solutions of chromic acid Ostwald concludes that the dissolved acid is present as dichromic acid, $H_2Cr_2O_7$.[2] On the other hand Costa considers that a solution of chromium trioxide contains the acids $H_2Cr_2O_7$ and H_2CrO_4.[3]

Chromic acid in its chemical properties resembles sulphuric acid, and the normal salts are usually isomorphous with the corresponding sulphates. The constitution of chromic acid is represented by the formula $CrO_2(OH)_2$, and the hydroxyl groups may be replaced by halogens and other radicals, such as the amido-group, giving rise to substances analogous to those derived in a similar manner from sulphuric acid. In the same way dichromic acid and the dichromates correspond to disulphuric acid and the disulphates; thus the former have the constitution represented by the formula $(OH)CrO_2{\cdot}O{\cdot}CrO_2(OH)$, and the hydroxyl groups in these compounds may also be replaced by other simple or compound radicals. In addition, salts are also known containing three and four molecules of chromium trioxide to one molecule of basic oxide; these are known as the *trichromates* and *tetrachromates*, and their constitution is represented by the formulæ $(M^IO)CrO_2.O.CrO_2.O.CrO_2(OM^I)$, and $(M^IO)CrO_2.O.CrO_2.O.CrO_2.O.CrO_2(OM^I)$.

Normal Potassium Chromate, K_2CrO_4, is obtained by the addition of potash to a solution of the dichromate. On evaporating the solution yellow rhombic pyramids crystallise out, which are isomorphous with potassium sulphate, and crystallise with the latter salt in all proportions. It has a

[1] Moissan, *Compt. rend.*, 1884, **98**, 1581.
[2] *Zeit. physikal. Chem.*, 1888, **2**, 78.
[3] *Gazz.*, 1906, **36**, i., 535.

specific gravity of 2·71 at 3·9°, and does not undergo alteration in the air. On heating, it becomes red-coloured, and melts at a high temperature without decomposition, solidifying on cooling to a crystalline mass. It dissolves in water with a yellow colour which is perceptible even when very small quantities of the substance are present, one part of the salt imparting a distinct yellow tint to 400,000 parts of water. One hundred parts of water dissolve :[1]

At	0°	30°	60°	105·8°
K_2CrO_4	54·57	65·13	74·60	88·8 parts.

The saturated solution boils at 105°. The salt has a bitter cooling taste and an alkaline reaction. On evaporating its solution red crystals of the dichromate are first deposited and afterwards the yellow crystals of the neutral sort. It is decomposed by all acids, even by carbonic acid with formation of the dichromate. It is insoluble in alcohol.

Potassium Dichromate, or *Bichromate of Potash*, $K_2Cr_2O_7$, serves as the starting point for the preparation of almost all the other chromium compounds, and is prepared on the large scale from chrome iron ore.

Up to the year 1820 potassium dichromate was used only for the purpose of making chrome yellow, and was prepared by the calcination of chrome iron ore with costly saltpetre. In the above year Köchlin introduced potassium dichromate into the process of Turkey-red dyeing, and it was soon employed for a variety of other purposes, especially in wool dyeing. In its preparation potashes were employed instead of saltpetre, and the chrome iron stone was oxidised in reverberatory furnaces by means of atmospheric oxygen. An important improvement was made in the process by Stromeyer by the introduction of a certain quantity of lime together with the potash. Not only was a saving of alkali thus effected, but the oxidation was rendered easier, inasmuch as the whole mass did not fuse, and therefore remained porous and more capable of absorbing the atmospheric oxygen. The chrome iron ore is first roasted and 4½ parts of the finely ground ore mixed with 2¼ parts of potassium carbonate and 7 parts of lime. This mass after drying at 150° is heated to bright redness with an oxidising flame, the whole being constantly stirred. At the end of the operation the charge is withdrawn from the furnace, and, after

[1] Koppel and Blumenthal, *Zeit. anorg. Chem.*, 1907, **53**, 262.

cooling, is lixiviated with the minimum amount of hot water. If calcium chromate be found in solution a hot saturated solution of potassium sulphate is added, when the calcium is thrown down as sulphate and potassium chromate remains in solution. The liquor is next treated with the requisite quantity of sulphuric acid, diluted with twice its volume of water, to convert the chromate into dichromate, and then allowed to cool. The solution of chromate saturated at 16° contains nearly 1 part of salt to 2 parts of water, whilst the dichromate requires 10 parts of water for its solution; hence when the saturated solution of chromate is converted into dichromate, a precipitate of about three-quarters of the dichromate will be formed on cooling. The precipitate is collected and then recrystallised. The mother-liquor, which contains potassium sulphate, is used for the lixiviation of another portion of the roasted mass.

This salt may be prepared also by electrolysing a solution of caustic potash using an anode of ferrochrome and a cathode of porous copper oxide.[1]

Potassium dichromate crystallises in splendid garnet-red tablets or prisms belonging to the triclinic system, having a specific gravity of 2·692 at 3·9°. It melts below a red heat, forming a transparent red liquid, which when slowly cooled solidifies in crystals which have the same form as those deposited from aqueous solution. It decomposes at a white heat into oxygen, chromic oxide, and the normal salt. One hundred parts of water dissolve :[2]

At	0°	30°	60°	104·8°
$K_2Cr_2O_7$	4·64	18·13	45·44	108·2 parts.

The saturated solution boils at 104·8°. Potassium dichromate has an acid reaction, a cooling, bitter, metallic taste, and is insoluble in alcohol; it acts as a powerful poison, probably on account of its oxidising properties. The commercial salt is usually almost chemically pure, and is employed for the preparation of the other chromium compounds, as a reagent, and as an oxidising agent, as well as being largely used in dyeing and calico-printing.

A film of organic matter saturated with a solution of potassium dichromate acquires a dark colour on exposure to

[1] Lorenz, *Zeit. anorg. Chem.*, 1896, **12**, 396.

[2] Koppel and Blumenthal, *Zeit. anorg. Chem.*, 1907, **53**, 262.

light, owing to a reduction to chromic oxide taking place, and a solution of this substance in gelatine is used as a sensitive agent in the Autotype and other similar *photographic printing* processes. These processes depend not merely upon the de-oxidation of the dichromate, but also upon the fact that this reduction renders the gelatine insoluble in, and non-absorbent of, water, so that those portions of the gelatine film which have been acted upon by the light remain unchanged when the film is immersed in hot water, while those parts which have been protected from the action of the light dissolve away entirely. A film is thus obtained in which the various shades of the original negative are represented by deposits of varying thickness of the insoluble gelatine, which can be coloured with any desired pigment; in this way the red or blue chalk drawings of the old masters can be produced in exact fac-simile.[1]

Potassium dichromate forms a double salt with mercuric chloride, $K_2Cr_2O_7,HgCl_2$, which separates out in red well-developed rhombic crystals.

Potassium Trichromate, $K_2Cr_3O_{10}$, is formed by the action of chromic acid solution on the dichromate, but is best prepared by boiling the dichromate with nitric acid of specific gravity 1·19; on cooling, potassium nitrate first separates almost completely, and the decanted liquor then deposits the trichromate in deep-red monoclinic prisms, having a specific gravity of 2·648. It is decomposed by hot water into chromic acid and the dichromate, and cannot therefore be recrystallised in this manner.[2]

Potassium Tetrachromate, $K_2Cr_4O_{13}$, is obtained by heating the dichromate with nitric acid of specific gravity 1·41, and separates out on cooling in brownish-red crusts consisting of small rhombic plates. It has a specific gravity of 2·649, and, like the trichromate, is decomposed by water into chromic acid and the dichromate. The compound described by Darmstädter as potassium nitrochromate is identical with the tetrachromate.[3]

Normal Sodium Chromate, $Na_2CrO_4,10H_2O$.—Is obtained by fusing chromic oxide and sodium nitrate together, and evaporating the solution at a low temperature, or by allowing a

[1] For a full and interesting description of these processes, see Abney's *Treatise on Photography*. (Longmans.)

[2] Jäger and Krüss, *Ber.*, 1889, **22**, 2038.

[3] Wyrouboff, *Bull. Soc. chim.*, 1881, [2], **35**, 162

solution of potassium chromate saturated with soda to evaporate at 0°. The salt is deposited in deliquescent transparent yellow prisms, isomorphous with Glauber's salt. When the solution is heated to above 30° the anhydrous salt separates out. It has an alkaline reaction, and a bitter metallic taste. Hydrates containing $4H_2O$ and $6H_2O$ have also been obtained.[1]

Sodium Dichromate, $Na_2Cr_2O_7,2H_2O$, crystallises in thin triclinic yellowish-red deliquescent prisms. This salt is now manufactured on a large scale; it is much more soluble than the potassium salt, and for this reason is used as a depolariser in chromic acid cells in place of the potassium salt.

Ammonium Chromate, $(NH_4)_2CrO_4$.—This salt can be obtained pure only from solutions containing excess of ammonia, as it readily loses the latter, forming the dichromate. It is obtained in golden-yellow monoclinic needles, by gently warming pure chromium trioxide with a quantity of ammonia of specific gravity 0·90, which is just sufficient to dissolve the chromate formed, and cooling the solution in a freezing mixture. The *dichromate*, $(NH_4)_2Cr_2O_7$, is readily obtained by adding the requisite quantity of chromium trioxide to ammonia, and separates out on evaporation in orange-red monoclinic crystals, having a specific gravity of 2·367. These are stable in the air, but decompose on ignition into nitrogen, water, a bulky leaf-like mass of chromium sesquioxide, and generally a little ammonia. This salt forms a number of crystalline double salts with mercuric chloride.[2] The *trichromate* and *tetrachromate* have also been prepared.

474 Most of the other metals form chromates or basic chromates which are for the most part coloured substances insoluble in water, many of which are largely used as pigments. The most important of these are the following:

Copper Chromates.—Copper Dichromate, $CuCr_2O_7,2H_2O$, is obtained by the action of concentrated chromic acid solution on copper hydroxide. It forms blackish-brown deliquescent crystals. The solution when boiled deposits the basic salt $Cu_3CrO_6,2H_2O$ as a brown precipitate, which is also obtained when boiling solutions of normal potassium chromate and copper sulphate are mixed. Cold solutions, on the other hand, yield the double salt $K_2CrO_4,Cu_3Cr_2O_9,2H_2O$, which is obtained also by the action of potassium dichromate solution on freshly

[1] Salkowski, *Ber.*, 1901, **34**, 1947.
[2] Jäger and Krüss, *Ber.*, 1889, **22**, 2047.

precipitated copper hydroxide in pale-brown microscopic six-sided tablets. The mineral vauquelinite, $(Cu,Pb)_3Cr_2O_9$, occurs in small glistening monoclinic crystals or earthy masses, together with crocoisite.

Silver Chromate, Ag_2CrO_4, is obtained as a brick-red amorphous precipitate when a solution of potassium chromate is poured into excess of a concentrated solution of silver nitrate either cold or hot.[1] It is formed when silver dichromate is boiled for a long time with water as a deep green crystalline powder, which is insoluble in water, but dissolves with some difficulty in sulphuric acid, nitric acid, and ammonia. The solution obtained by dissolving it in as small a quantity as possible of warm ammonia of specific gravity 0·94 deposits ammonio-silver chromate, $Ag_2CrO_4,4NH_3$, on cooling in long yellow needles belonging to the tetragonal system.[2]

The red chromate may be converted into the green form by heating in an atmosphere of carbon dioxide (Autenrieth).

Silver Dichromate, $Ag_2Cr_2O_7$, is obtained by the action of potassium dichromate on silver nitrate in acid solution; it forms small red triclinic crystals, which are decomposed by boiling water into chromic acid and the normal chromate. It may also be obtained by warming silver chromate with dilute nitric acid.[3]

Barium Chromate, $BaCrO_4$, is an insoluble yellow precipitate, having a specific gravity of 3·9. It is insoluble in acetic, but easily soluble in nitric, hydrochloric, and aqueous chromic acids. From the last solvent the salt $BaCr_2O_7,2H_2O$ may be obtained in yellow stellar needles, which are decomposed by water with separation of the normal salt. Barium chromate is used as a pigment under the name of *yellow ultramarine* or *lemon chrome*. It is, however, now very little used, as the lead chromates have a brighter colour and more body.

Zinc Chromates.—Potassium chromate gives with zinc sulphate a yellow precipitate of basic zinc chromate, $Zn_2(OH)_2CrO_4,H_2O$. A similar compound, $2Zn_2(OH)_2CrO_4,H_2O$, is formed when zinc carbonate is heated with a solution of chromic acid.

If zinc oxide or a zinc salt is boiled with potassium dichromate the yellow insoluble compound, $Zn_4(OH)_6CrO_4$, is precipitated.

[1] Autenrieth, *Ber.*, 1902, **35**, 2057.
[2] Muthmann, *Ber.*, 1889, **22**, 2051.
[3] Autenrieth, *Ber.*, 1902, **35**, 2059.

The chromate obtained by the addition of a hot neutral solution of zinc sulphate to potassium chromate forms a stable yellow pigment sold under the name of *Zinc yellow* or *Buttercup yellow.*

Lead Chromate, $PbCrO_4$, occurs as crocoisite in translucent yellow monoclinic prisms, having a specific gravity of 5·9 to 6·1. The mineral is found in Siberia, in the Urals, Brazil, Hungary, and the Philippine islands. Crystals having a specific gravity of 6·118 are artificially obtained when lead chloride is strongly heated with potassium chromate, as well as when solutions of lead acetate and normal potassium chromate are allowed slowly to diffuse into one another.[1] A bright yellow precipitate of the normal chromate is obtained when a solution of a lead salt is precipitated with potassium dichromate. This goes under the name of *chrome yellow, Paris yellow,* or *Leipsic yellow,* and is largely used as a pigment. It is insoluble in water, but is readily dissolved by nitric acid and caustic potash. When strongly heated it fuses to a brown liquid, which on cooling solidifies to a crystalline mass. As lead chromate at a red heat oxidises all organic substances, it is frequently employed in organic analysis, especially in the case of bodies which contain chlorine, sulphur, &c. The chrome yellow of commerce often contains admixtures, especially lead sulphate. This, however, is not always to be considered as an adulteration, and it is used for the preparation of a light shade. This is termed *Cologne yellow,* and is obtained by the precipitation of a mixture of the nitrates of lead and calcium with a mixture of sodium sulphate and potassium chromate, or more generally by heating lead sulphate with a solution of potassium dichromate.

Calico is printed or dyed with chrome yellow, by first mordanting the cloth with a solution of lead salt, and afterwards steeping it in one of potassium chromate.

Basic Lead Chromate, Pb_2CrO_5, occurs in commerce as *chrome red,* and is obtained as a fine red powder by digesting chrome yellow with cold caustic soda, boiling it with a solution of normal potassium chromate, or fusing it with nitre. Another basic salt, $Pb_3Cr_2O_9$, occurs as the mineral phœnicite, in hyacinth-red crystals, having a specific gravity of 5·75. It may be artificially prepared together with the normal chromate by allowing solutions of lead nitrite and potassium

[1] Drevermann, *Annalen,* 1853, **87**, 121.

chromate to diffuse into one another, when it separates in dark-red tablets.

By making a suitable mixture of chrome yellow and chrome red, or by modifying the process of manufacture so as to obtain a mixture of these, pigments of any shade between the two may be obtained. These are known commercially as *chrome orange.*

Bismuth Chromate.—When normal potassium chromate is added to a solution of bismuth nitrate a lemon-yellow finely crystalline precipitate is thrown down, having the composition $Bi_6Cr_2O_{15} = 2(BiO)_2CrO_4,Bi_2O_3$. This compound does not fuse, and is not decomposed on heating. When treated with a quantity of nitric acid insufficient to dissolve it, it is converted into $Bi_2Cr_2O_9 = (BiO)_2Cr_2O_7$; this salt is obtained also by adding a solution of bismuth nitrate, as nearly as possible neutral, to an excess of a solution of potassium dichromate. It is an orange-yellow crystalline powder which decomposes on ignition and becomes of a dark-green colour. If a few drops of nitric acid are added to the liquid after precipitation, and the whole boiled for a few hours, a cinnabar-red crystalline salt, $(BiO)_2CrO_4$, is thrown down, which partially dissolves on boiling with moderately strong nitric acid, and is partially converted into ruby-red crystals having the formula $Bi_2Cr_4O_{15},H_2O$.[1] Other polychromates of bismuth have been prepared.[2]

Chromic Chromate, $Cr_2O_3,CrO_3 = 3CrO_2$.—This compound, also known as *chromium dioxide,* is formed when chromic nitrate is gently heated. It is likewise prepared by the partial reduction of the trioxide, and by the precipitation of a chromic salt with a soluble chromate. The brown powder thus obtained is easily soluble in acids. Alkalis precipitate chromic hydroxide from its solution, whilst a chromate remains in the liquid. If chromic chromate be washed for some time with water, it is decomposed into soluble trioxide and insoluble sesquioxide. When nitric oxide is passed into a tolerably concentrated solution of potassium dichromate, chromic chromate is obtained as a dark-brown precipitate, which dries at 250° to form a black hygroscopic powder, and this, when heated in a current of hydrogen chloride, yields chromic oxide, water, and chlorine.

[1] Muir, *Journ. Chem. Soc.*, 1876, ii., 12.
[2] *Journ. Chem. Soc.*, 1877, i., 24, 645.

A hygroscopic black powder has also been obtained by Manchot and Kraus[1] by heating chromic hydroxide in a current of oxygen. This contains a little water, which it gives off at a red heat along with some of its oxygen, chromic oxide, Cr_2O_3, being left. When washed with water no chromium trioxide is obtained, and these investigators therefore consider it to be a dioxide, CrO_2, and not chromic chromate.

When the vapour of chromic chloride is passed through a red-hot tube, violet translucent prisms, having the composition $Cr_5O_9 = 2Cr_2O_3,CrO_3$, are obtained. These are magnetic, and on ignition are gradually converted into chromic oxide.[2]

A number of crystalline double chromates have been described which have the general formula $M^I_2M^{II}(CrO_4)_2,6H_2O$, where $M^I = K$, Rb, NH_4, or Cs, and $M^{II} = Ni$, Mg, or Cd, as well as ammoniacal double chromates of the formula $M^I_2M^{II}(CrO_4)_2,2NH_3$, where $M^I = K$ or NH_4, and $M^{II} = Cu$, Zn, Cd, Ni, or Co.[3]

Halogen and Amido-derivatives of Chromic Acid.

475 *Chromyl Difluoride*, CrO_2F_2.—This substance was first obtained by Unverdorben, by the action of sulphuric acid on a mixture of lead chromate and fluorspar, and was regarded by him as chromium hexafluoride. Olivieri has, however, shown that it contains only two atoms of fluorine to one of chromium, and is in reality derived from chromic acid by the replacement of the two hydroxyl groups by fluorine. It is best prepared by heating 60 grams of well-dried potassium dichromate and 30 grams of fluorspar with 100 grams of fuming sulphuric acid in a platinum retort. It condenses in a freezing mixture to a blood-red, very volatile liquid, which is converted even by the moisture of the air into chromic fluoride and chromic acid.

Potassium Fluochromate, $F.CrO_2.OK$, is formed by heating potassium dichromate with hydrofluoric acid in a platinum vessel, and crystallises in red tetragonal pyramids, which are soluble in water. The solution decomposes on boiling into potassium dichromate and hydrofluoric acid.

Chromyl Dichloride, CrO_2Cl_2, appears to have been discovered by Thomson,[4] and was then investigated by Berzelius and

[1] *Ber.*, 1906, **39**, 1352; see also Meerburg, *Zeit. anorg. Chem.*, 1907, **54**, 31.
[2] Geuther, *Annalen*, 1861, **118**, 61.
[3] Briggs, *Journ. Chem. Soc.*, 1903, **83**, 391; 1904, **85**, 672, 677.
[4] *Phil. Trans.*, 1827, **117**, 159.

Wöhler.[1] It is prepared by distilling a fused mixture of ten parts of common salt and twelve parts of potassium dichromate, with thirty parts of concentrated sulphuric acid, and, in order to remove free chlorine, repeatedly rectifying the distillate in a current of carbon dioxide. It is also formed by heating chromium trioxide in a current of hydrogen chloride, when it distils over, and an oily liquid remains which probably is *chlorochromic acid*, $Cl.CrO_2.OH$. It may readily be obtained by dissolving chromic acid in concentrated hydrochloric acid, and adding sulphuric acid to the cooled liquid in small quantities at a time. The heavier chromyl chloride is then run off, dry air is blown through, and the liquid distilled.[2] Chromyl dichloride is a mobile liquid of a splendid blood-red colour by transmitted, and nearly black by reflected light. It boils at 115·9°, and has a specific gravity at 25° of 1·920.[3] It absorbs chlorine readily, dissolves iodine, and when dropped into water it remains unaltered for a few seconds, but is afterwards decomposed with violent ebullition into chromic and hydrochloric acids. The specific gravity of the vapour of chromyl dichloride is, according to Bineau, 5·39, corresponding to the above formula. When brought into contact with phosphorus it explodes, whilst it takes fire in contact with sulphur, hydrogen sulphide, ammonia, alcohol, and many other organic bodies, and when diluted with acetic acid or carbon tetrachloride, acts as an oxidising and chlorinating agent upon hydrocarbons. When chromyl dichloride is heated in a closed tube to 180° for three or four hours, *trichromyl chloride*, $Cr_3O_6Cl_2$, is formed as a black powder, which deliquesces on exposure to the air.[4]

Bromine and iodine do not form analogous chromyl derivatives, but when a bromide or iodide is heated with sulphuric acid and potassium dichromate, free bromine or iodine is obtained. This reaction is made use of for the qualitative detection of chlorine in presence of bromine or iodine, as if chlorine be present the substance yields chromyl chloride when heated with potassium dichromate and sulphuric acid, and the latter by the action of water is converted into chromic acid, which may be recognised by the usual tests.

Potassium Chlorochromate, $Cl.CrO_2.OK$, was discovered by

[1] *Pogg. Ann.*, 1834, **33**, 343.
[2] Law and Perkin, *Journ. Chem. Soc.*, 1907, **91**, 191.
[3] Thorpe, *Journ. Chem. Soc.*, 1880, **37**, 327.
[4] *Journ. Chem. Soc.*, 1870, **23**, 31.

Péligot,[1] and is formed when three parts of potassium dichromate are gently heated with four parts of concentrated hydrochloric acid and a small quantity of water, or when chromyl dichloride is added to a saturated solution of potassium chloride:

$$CrO_2Cl_2 + KCl + H_2O = KCrO_3Cl + 2HCl.$$

It crystallises in flat red rectangular prisms, having a specific gravity of 2·497. The salt is partially decomposed by water, but may be recrystallised from water containing hydrochloric acid. It decomposes at 100°, with evolution of chlorine:

$$4CrO_2(OK)Cl = K_2Cr_2O_7 + Cr_2O_3 + 2KCl + Cl_2 + O_2.$$

Other chlorochromates have been described by Péligot and by Prætorius.[2]

Potassium Amidochromate, $NH_2.CrO_2.OK$, is formed by passing ammonia into ether containing the chlorochromate in suspension. After 24 hours the product is dissolved in water, filtered from an insoluble substance simultaneously formed, and the solution evaporated. The amidochromate crystallises out in garnet-red monoclinic prisms, which are only slowly decomposed by boiling water, and somewhat more rapidly by caustic potash. On treatment with nitrous acid it yields nitrogen and potassium dichromate:

$$2CrO_2(OK)NH_2 + 2HNO_2 = 2N_2 + 3H_2O + K_2Cr_2O_7.$$

When an aqueous solution of the amidochromate is treated with chlorine in the presence of ammonia, the whole being covered with a layer of ether, a light-brown ethereal solution is obtained which deposits yellowish-brown leaflets of *chromylamide*, $CrO_2(NH_2)_2$.[3]

Perchromic Acid and the Perchromates.—A deep indigo-blue coloured solution is obtained when hydrogen peroxide is added to an aqueous solution of chromium trioxide, or to a solution of a chromate acidified with sulphuric acid. If the freshly prepared solution be shaken with ether, this liquid takes up the perchromic acid and becomes of a dark-blue colour. The ethereal is more stable than the aqueous solution, but on evaporation it leaves a residue of chromium trioxide. The same decomposition is effected by alkalis, a chromate being formed with evolution of oxygen. The colouring power of

[1] *J. Pharm.*, 1833, **19**, 301.
[2] *Annalen*, 1880, **201**, 1.
[3] Ohly, *Chem. News*, 1899, **80**, 134.

perchromic acid is so great that its formation is employed as a most delicate test, both for chromic acid and for hydrogen peroxide. The deepest coloration is produced when two molecules of hydrogen peroxide are used to one molecule of chromium trioxide.

The constitution of the substance thus formed is as yet uncertain. It has been variously regarded as Cr_2O_7,xH_2O,[1] $CrO_6,3H_2O$,[2] CrO_3,H_2O_2,[3] and $2HCrO_4,H_2O_2$,[4] &c. By the action of sodium peroxide on a thin paste of chromic hydroxide and water Häussermann[5] obtained a sodium salt having the composition $Na_6Cr_2O_{15},28H_2O$, which would be the salt of an acid derived from the anhydride CrO_6. When this salt is treated with sulphuric acid, the above characteristic blue colour is first produced, but oxygen is soon evolved, and chromic sulphate remains in solution. Salts of a perchromic acid, $HCrO_5$, with pyridine, quinoline, and other organic bases have been prepared by Wiede,[6] by adding the bases to the blue ethereal solution of perchromic acid cooled below 0°. These are explosive crystalline compounds, which evolve oxygen when treated with strong acids. In a similar manner he has obtained blue potassium and ammonium salts, which he regards as $(NH_4)CrO_5,H_2O_2$ and $KCrO_5,H_2O_2$, the hydrogen peroxide acting like water of crystallisation. On the other hand, according to Riesenfeld,[7] the last two compounds are acid salts of the perchromic acid, H_3CrO_7, and have, therefore, formulæ of the type $R^IH_2CrO_7$ The same compounds are formed by the action of hydrogen peroxide on chromates in cold, faintly acid solution, whilst in alkaline solution red salts of a perchromic acid, H_3CrO_8, are obtained. The red ammonium salt, $(NH_4)_3CrO_8$, when treated with dilute acids, gives off oxygen and forms the blue salt $(NH_4)H_2CrO_7$, and both these compounds yield with pyridine Wiede's pyridine salt of the acid $HCrO_5$; finally, all three compounds, on treatment with excess of ammonia, form

[1] Barreswil, *Ann. Chim. Phys.*, 1847, [3], **20**, 364.

[2] Fairley, *Chem. News*, 1876, **33**, 337.

[3] Moissan, *Compt. rend.*, 1883, **97**, 96.

[4] Berthelot, *Compt. rend.*, 1889, **108**, 25.

[5] *J. pr. Chem.*, 1893, (2), **48**, 70.

[6] *Ber.*, 1897, **30**, 2178: 1898, **31**, 3139, 516; 1899, **32**, 378; see also Hofmann and Hiendlmaier, *ibid.*, 1905, **38**, 3059.

[7] *Ber.*, 1905, **38**, 4068; 1908, **41**, 2826; 1911, **44**, 147; *Zeit. anorg. Chem*, 1912, **74**, 48; compare Hofmann and Hiendlmaier, *Ber.*, 1904, **37**, 1663.

triammine chromium tetroxide, $CrO_4,3NH_3$. This compound is a brown crystalline substance which has the specific gravity 1·964 at 15·8°, and explodes on heating.[1]

Riesenfeld considers that when excess of hydrogen peroxide acts on a solution of chromic acid, the acid, H_3CrO_8, is mainly produced, but at the same time a little of the acid, H_3CrO_7, is also formed, whilst the blue ethereal solution probably contains a mixture of several perchromic acids.[2]

Chromous Salts.

476 *Chromous Chloride*, $CrCl_2$, is formed by the ignition of chromium in hydrogen chloride, or of chromic chloride in a current of hydrogen gas free from oxygen, and forms white, silky, lustrous needles which are stable in dry air. It dissolves in water, with evolution of heat, forming a blue solution, which absorbs oxygen with extreme avidity yielding basic chromic salts, and forms a powerful reducing agent. This solution is best obtained as follows: 300—400 grams of amalgamated granulated zinc and 50 grams of very finely powdered potassium dichromate are placed in a flask of about 3 litres capacity, and a mixture of 300 c.c. of pure fuming hydrochloric acid and 200 c.c. of water added. A violent reaction occurs, the liquid becoming first green from the intermediate formation of chromic salts, but after a few minutes a clear sky-blue solution remains, which may be directly employed as a reducing agent or for absorbing oxygen. To obtain pure chromous chloride from the solution, sodium acetate is added to the liquid, the precipitated chromous acetate washed with water saturated with carbon dioxide, redissolved in hydrochloric acid, and a current of hydrogen chloride passed into the cooled solution. All these operations must be performed in an atmosphere free from oxygen. The chromous chloride is thus obtained in blue needles containing 4 molecules of water.[3]

The vapour density of chromous chloride at 1300° was found by Nilson and Pettersson to be 7·8, considerably lower than is required by the formula Cr_2Cl_4. At 1600° the density is further

[1] Wiede, *Ber.*, 1897, **30**, 2178; 1899, **32**, 378; Riesenfeld, Wohlers, Kutsch and Ohl, *Ber.*, 1905, **38**, 1885, 3380.

[2] See also Spitalsky, *Zeit. anorg. Chem.*, 1907, **53**, 184; 1907, **54**, 265; 1907, **56**, 72; 1910, **69**, 179; *Ber.*, 1910, **43**, 3187.

[3] Recoura, *Ann. Chim. Phys.*, 1887, [6], **10**, 9.

reduced to 6·2, showing that probably at a higher temperature its density would finally reach 4·25, corresponding to $CrCl_2$.[1]

Chromous Bromide, $CrBr_2$, is obtained by gently heating chromic bromide in hydrogen gas, and also by heating the metal in gaseous hydrobromic acid. It is a white, crystalline mass, yielding a green basic chromic bromide on exposure to the air.

Chromous Iodide, CrI_2, is a crystalline mass obtained by heating chromium in gaseous hydriodic acid.[2]

Chromous Sulphide, CrS, is obtained by igniting chromous chloride in sulphuretted hydrogen, or by the long continued heating of chromic sulphide in hydrogen, and forms a black powder which is attacked only with difficulty by acids.[3] It may also be prepared by heating chromium to a very high temperature in sulphuretted hydrogen, when it is obtained in prismatic needles having a specific gravity of 4·08, and sufficiently hard to scratch quartz.[4]

Chromous Sulphate, $CrSO_4,7H_2O$, is prepared by dissolving the metal in dilute sulphuric acid. It is best obtained by dissolving chromous acetate in dilute sulphuric acid; on cooling it separates out in fine blue crystals isomorphous with ferrous sulphate. The ammoniacal solution absorbs oxygen, nitric oxide and acetylene. If potassium sulphate be dissolved in a cold saturated solution of the chloride, alcohol added until a precipitate begins to form, and the mass allowed to stand for some weeks in absence of air, fine blue rhombic prisms, having the composition $K_2SO_4,CrSO_4,6H_2O$, are deposited; these soon become green on exposure to the air owing to absorption of oxygen.

Chromous Carbonate, $CrCO_3$, is obtained by precipitating the chloride with potassium carbonate. A yellow to greenish-blue precipitate is obtained in the cold, and this assumes a reddish-brown colour on warming. Several double salts of chromous carbonate with the alkali carbonates have been prepared by the action of carbon dioxide on a mixture of solutions of chromous acetate and the alkali carbonate,[5] These are powerful reducing agents, and decompose water at 100°.

Chromous Acetate is a red crystalline precipitate obtained by

[1] *Journ. Chem. Soc.*, 1888, **53**, 830.
[2] Moissan, *Compt. rend.*, 1891, **92**, 1051.
[3] Moissan, *Compt. rend.*, 1880, **90**, 817.
[4] Mourlot, *Compt. rend.*, 1895, **121**, 943.
[5] Baugé, *Compt. rend.*, 1896, **122**, 474; 1897, **125**, 1177; 1898, **126**, 1566.

pouring a solution of chromous chloride into a saturated solution of sodium acetate.

Chromic Salts.

477 The normal chromic salts have a blue or violet colour, and allow red light to pass through their solutions. The cold solutions have a violet colour, which on heating changes to green; in some cases the solution immediately becomes violet on cooling, but in others this occurs only on allowing the cooled solution to stand for some time. Only the violet solutions of the salts with oxy-acids yield crystalline salts, the green solutions depositing an amorphous mass on evaporation. Many attempts have been made to explain the changes which take place, and much light has been thrown on the subject by the researches of Recoura and others. The salts which have been most closely examined are the chloride, bromide, and sulphate.

In the case of the chloride and bromide it appears that each exists in a violet and a green modification, both of which can be obtained crystalline, and combined with the same number of molecules of water; the former modification exists in dilute solutions and the latter in concentrated solutions, or in solutions containing an excess of acid. In addition, a different compound is obtained by dissolving the hydroxide, $Cr_2O(OH)_4$, in hydrochloric acid, and has probably the composition Cr_2OCl_4. In the case of the sulphate, and probably of the other oxy-acid salts the green solution contains complex derivatives of this same hydroxide, $Cr_2O(OH)_4$ (p. 1046).

Chromium and the Halogens.

478 *Chromic Fluoride*, CrF_3.—The anhydrous salt is obtained by passing hydrogen fluoride over heated chromic chloride, and sublimes at a high temperature in slender needles. The crystalline hydrate, $CrF_3,9H_2O$, is obtained by adding ammonium fluoride to a cold solution of chromic sulphate. It is sparingly soluble in water, but dissolves in hydrochloric acid, forming a violet solution. When heated in the air it becomes green, and finally leaves a residue of chromium trioxide.[1]

Chromic Chloride, $CrCl_3$.—The anhydrous chloride is obtained by heating an intimate mixture of chromic oxide and carbon in

[1] Poulenc, *Compt. rend.*, 1891, **116**, 253; Fabris, *Gazz.*, 1890, **20**, 582.

a stream of dry chlorine. It forms peach-blossom coloured scales, which have a specific gravity of 3·03. These volatilise at 1065°, yielding a vapour of the density 6·135, the formula $CrCl_3$ requiring 5·478, and Cr_2Cl_6 corresponding to a density twice as great; hence this latter compound cannot exist in the state of vapour. From 1190° up to 1300° the density is 5·5 (Nilson and Pettersson). Chromic chloride is almost insoluble in cold water, but it is readily soluble in presence of a very small quantity (less than 0·001 per cent.) of chromous chloride, cuprous chloride, stannous chloride, or other reducing agents.[1] The dilute solutions of the chloride have a violet colour, whilst the concentrated solutions or those containing a large excess of acid are green. Recoura[2] has shown that the heat evolved by the action of an equivalent quantity of soda is nearly 50 per cent. greater in the case of the green solutions, and that as the concentration of the solution increases, the evolution of heat gradually increases from the value for the violet solution (+22·2 cal.) to that for the green (+31·5 cal.). The colour of the solution at the same time gradually changes from violet to pure green, thus indicating a gradual transition of the violet into the green modification. It has also been shown[3] that equilibrium between the green and the violet salts is set up in solution, either salt leading to the same final conditions, depending on the concentration. In dilute solutions the salt is almost all present in the violet form, whilst as the concentration increases the equilibrium shifts more and more in favour of the green. The equilibrium is reached very slowly at ordinary temperatures, but may be attained in 24 hours at 84°. Both modifications have been isolated in the crystalline condition by Recoura, and both have the same composition, $CrCl_3,6H_2O$.[4]

The green chloride separates out in small, emerald-green crystals when a current of hydrogen chloride is passed through a well-cooled, saturated solution of chromic chloride. If the crude chloride be dissolved in its own weight of water, warmed for a few minutes to 80°, and then cooled to 0°, the solution

[1] Rohland, *Zeit. anorg. Chem.*, 1899, **21**, 37; Drucker, *Zeit. physikal. Chem.*, 1901, **36**, 173.

[2] Recoura, *Ann. Chim. Phys.*, 1887, [6], **10**, 5.

[3] Roozeboom and Olie, *Proc. K. Akad. Wetensch. Amsterdam*, 1905, **8**, 66; *Zeit. anorg. Chem.*, 1906, **51**, 29; Werner and Gubser, *Ber.*, 1901, **34**, 1379.

[4] Marchetti, *Gazz.*, 1882, **22**, 375.

contains both green and violet salt, and on passing in hydrogen chloride, only the latter separates out at first and may be obtained free from the green modification if it be immediately filtered off. It forms greyish-blue crystals which dissolve in water, forming the characteristic blue-violet solution. Both of the salts immediately react with three equivalents of soda yielding one and the same chromic hydroxide. A third isomeride has been obtained by Bjerrum[1] by adding ether saturated with hydrogen chloride to the solution left after precipitating the violet salt with hydrochloric acid. Recoura's green salt when kept in a desiccator loses two molecules of water, forming a green hydrate, $CrCl_3.4H_2O$, whilst a decahydrate, $CrCl_3,10H_2O$, is also known.[2] The constitution of these hydrates will be discussed along with the ammoniacal compounds of chromium (p. 1054).

When hydrochloric acid acts on the hydroxide $Cr_2O(OH)_4$, a compound is obtained which has a less bright colour than the green salt described above. It reacts with only two equivalents of soda, and has therefore probably the composition Cr_2OCl_4, and corresponds to the green salts formed by heating the solutions of the salts of chromium derived from oxy-acids (p. 1046). In presence of hydrochloric acid it is slowly converted into one or other of the above trichlorides according to the concentration of the solution.

Double compounds of an oxychloride of chromium with the chlorides of the alkali metals have been described, in which the chromium appears to be pentavalent. Thus the potassium compound, $CrOCl_3,2KCl$, is formed as a garnet-red, crystalline precipitate when a solution of potassium chloride is added to a concentrated solution of chromic acid, which has previously been treated with hydrochloric acid at – 20°, and the mixture saturated at 0° with hydrochloric acid. Similar compounds have been prepared with the other alkali chlorides, and also with quinoline and pyridine hydrochlorides.[3]

Chromic Bromide, $CrBr_3$.—The anhydrous compound is prepared in a similar way to the chloride. It forms black, semi-metallic, translucent, hexagonal scales, having an olive-green colour, and exhibits in one direction a fine red dichroism.

[1] *Ber.*, 1906, **39**, 1599.

[2] Werner and Gubser, *Ber.*, 1901, **34**, 1379; Olie, *Zeit. anorg. Chem.*, 1907, **53**, 268.

[3] Weinland and Fridrich, *Ber.*, 1905, **38**, 3784; Weinland and Fiederer, *Ber.*, 1906, **39**, 4042; 1907, **40**, 2090.

In its properties it closely resembles the chloride, and dissolves easily in water, when a small quantity of chromous bromide, or any other reducing agent, such as tinfoil, is present. Solutions of chromic bromide behave in an analogous manner to those of the chloride, and yield two isomeric salts, the one forming blue-grey, and the other green crystals, both of which have the composition $CrBr_3,6H_2O$.[1]

Chromic Iodide is unknown.

Chromium and Sulphur.

479 *Chromium Sesquisulphide*, or *Chromic Sulphide*, Cr_2S_3.—This is obtained by heating chromium with sulphur, or by igniting chromic chloride, or the trioxide, in a current of hydrogen sulphide. It forms either a blackish-grey powder with a metallic lustre, or an elastic mass having a specific gravity of 3·77. When heated in the air it burns with formation of the green oxide, and in chlorine yields chloride of sulphur and chromic chloride. It is not attacked by nitric acid. This compound cannot be prepared in the wet way, as soluble sulphides precipitate the hydroxide from chromic salts, with liberation of sulphuretted hydrogen:

$$2CrCl_3+6H_2O+3(NH_4)_2S=2Cr(OH)_3+6NH_4Cl+3H_2S.$$

Chromic Sulphate, $Cr_2(SO_4)_3$, is obtained by mixing equal parts of concentrated sulphuric acid and chromium hydroxide dried at 100°. The mixture is allowed to stand in a loosely-stoppered bottle, when the solution, which, to begin with, is green, becomes blue, and in some weeks deposits a violet-blue, crystalline mass, which is purified by solution in water and precipitation with alcohol. Thus obtained, it is a violet, crystalline powder; if a smaller quantity of alcohol be added, blue octahedra containing 18 molecules of water are deposited. Chromic sulphate and the sulphates of the alkali metals form double salts, corresponding to the alums, to which the name of *chrome-alums* is given.

Potassium Chromic Sulphate, or *Chrome Alum*, K_2SO_4, $Cr_2(SO_4)_3,24H_2O$.—This substance is best obtained by the reduction of a solution of potassium dichromate, $K_2Cr_2O_7$, by adding the requisite quantity of sulphuric acid, and passing sulphur dioxide through the solution:

$$K_2Cr_2O_7+H_2SO_4+3SO_2=K_2SO_4+Cr_2(SO_4)_3+H_2O.$$

[1] Recoura, *Compt. rend.*, 1890, **110**, 1029.

In place of sulphur dioxide any other easily oxidisable substance, such as alcohol, &c., may be employed, but in this case more sulphuric acid must be added. Chrome alum is now obtained in large quantity as a by-product in the manufacture of artificial alizarine from anthracene, $C_{14}H_{10}$, in which the hydrocarbon is treated with a mixture of sulphuric acid and potassium dichromate, when anthraquinone, $C_{14}H_8O_2$, is formed, and this is then subjected to further treatment. The salt crystallises in large dark purple-red, almost black, octahedra, which, when seen by transmitted light, exhibit a ruby-red colour. It dissolves in seven parts of water at the ordinary temperature. The solution has a dingy blue colour, with a tinge of red, which when heated to 70° becomes dark green. After standing for several months, however, it returns to its ordinary colour (see below). Chrome alum is used in dyeing and calico-printing, as well as in tanning.

Ammonium Chromic Sulphate, $(NH_4)_2SO_4,Cr_2(SO_4)_3,24H_2O$, is obtained by crystallising a mixture of the two salts, or by reducing ammonium dichromate in presence of sulphuric acid. The salt is less soluble than the potassium compound, and crystallises readily in fine ruby-red octahedra, which have a specific gravity of 1·738.

A number of other crystalline double chromic sulphates, both anhydrous and containing water of crystallisation, have been described.[1]

Action of Heat on Chromic Sulphate and its Double Salts.— When the cold violet solution of chromic sulphate is boiled, or the crystals heated to 100°, a green salt is obtained, which, unlike the violet salt, is soluble in alcohol, and does not crystallise on evaporation. This change has been examined by many chemists, some of whom have attributed it to the formation of an isomeric modification, and others to the formation of a basic salt. As with the halogen derivatives, more complete investigations, especially those of Recoura, have thrown much light on the nature of the phenomenon. Recoura[2] has shown that in the boiled solution one-sixth of the sulphuric acid is in the free state, and that therefore the green salt formed has the empirical formula

[1] Klobb, *Compt. rend.*, 1893, **117**, 311; *Bull. Soc. chim.*, 1893, [3], **9**, 663.

[2] Recoura, *Ann. Chim. Phys.*, 1895, [7], **4**, 494; Favre and Valson, *Compt. rend.*, 1872, **74**, 1023; Whitney, *Zeit. physikal. Chem.*, 1896, **20**, 40; Dougal, *Journ. Chem. Soc.*, 1896, **69**, 1526; Colson, *Compt. rend.*, 1905, **140**, 42; 1907, **144**, 206.

$2Cr_2O_3,5SO_3$. When the recently boiled solution is treated with barium chloride in the cold, only one-third of the total sulphuric acid is precipitated as barium sulphate. As the whole of the free sulphuric acid would be thus precipitated, only one of the SO_3 groups in the above compound is precipitable as barium sulphate in the cold, and the remaining SO_3 groups must be combined with the chromium to form a complex basic radical of which the green salt is the sulphate. The change may be formulated as follows:

$$2Cr_2(SO_4)_3 + H_2O = [Cr_4O(SO_4)_4]''SO_4 + H_2SO_4.$$

In confirmation of this is the fact that the green salt, when treated with an excess of caustic soda, yields the hydroxide $Cr_2O(OH)_4$. The green salt may therefore be regarded as the sulphate of the hypothetical compound *sulphochromyl hydroxide*, $[Cr_4O(SO_4)_4](OH)_2$.

The above green salt is an unstable substance, and when the solution is allowed to stand in the cold it is gradually reconverted into the violet sulphate, from which the whole of the sulphuric acid may be precipitated by barium chloride in the cold, and which yields with caustic potash the trihydroxide, $Cr(OH)_3$.

The double salts, such as chrome alum, undergo an analogous reaction when their solutions are heated, and the solutions regain their violet colour on standing in the cold. It is probable that similar complex salts are formed in the case of the other chromic salts, as their solutions become green on boiling; but in these cases the compound formed is much less stable, and is immediately reconverted into the normal salt on cooling.

Green Modifications of Chromic Sulphate.—In addition to the above complex basic sulphate, a solid green salt of the same empirical formula as the normal violet salt is known, which, however, possesses entirely different properties.[1] This is obtained by heating the crystals of the violet salt, $Cr_2(SO_4)_3,18H_2O$, at 90° until they have the composition $Cr_2(SO_4)_3,8H_2O$.[2] The resulting green compound is readily soluble in water, but the freshly prepared solution shows neither the ordinary reactions of a chromium salt nor of a sulphate. In the course of a few days

[1] Recoura, *Ann. Chim. Phys.*, 1895, [7], **4**, 505.

[2] Compare Wyrouboff, *Bull. Soc. chim.*, 1902, **27**, 676; Colson, *Compt. rend.*, 1907, **144**, 206.

the solution is gradually transformed into the normal violet sulphate.

Several green chromium sulphates differing from this green salt of Recoura have been prepared by Colson [1] by the action of sulphur dioxide on chromic acid below 0°. Thus he has obtained a green salt, $Cr_2(SO_4)_3,6H_2O$, the freshly prepared solution of which does not react with barium sulphate, but rapidly changes into another green sulphate in which $\frac{1}{3}$ of the sulphuric acid is precipitable. This is gradually transformed into a third compound, which contains $\frac{2}{3}$ of its sulphuric acid in a precipitable state, and finally into violet chromium sulphate, when all the acid may be precipitated by barium chloride. This chemist has put forward the view that one molecule of water enters the molecule for each (SO_4) group that becomes precipitable, these divalent groups being thus replaced by the monovalent groups, (HSO_4) and (OH). Thus if the first green salt be represented by the formula $Cr_2(SO_4)_3$, the others are $Cr_2(SO_4)_2(OH)(HSO_4)$, $Cr_2(SO_4)(OH)_2(HSO_4)_2$, and the violet salt, $Cr_2(OH)_3(HSO_4)_3$. A cold solution of chromic sulphate contains all four salts in equilibrium.

Recoura's green sulphate combines with one, two, or three molecules of sulphuric acid, or with the equivalent quantities of a sulphate, yielding substances from which no barium sulphate can be obtained by precipitation in the cold; these may be regarded as the complex acids, *chromosulphuric acid*, $[Cr_2(SO_4)_4]H_2$, *chromodisulphuric acid*, $[Cr_2(SO_4)_5]H_4$, and *chromotrisulphuric acid*, $[Cr_2(SO_4)_6]H_6$, or their salts. These are quite stable in the dry state and in dry air, but in solution gradually undergo conversion into the normal chromium salts. The alkali chromosulphates are isomeric with the chrome alums, from which they may be readily obtained by heating the crystals of the latter for some time at 90°. *Potassium chromosulphate*, $[Cr_2(SO_4)_4]K_2,4H_2O$, is thus obtained as a green salt which dissolves slowly but completely in cold water. An analogous series of acids has been prepared by the union of Recoura's green sulphate with chromic acid. These have the compositions $Cr_2(SO_4)_3,CrO_4H_2$; $Cr_2(SO_4)_3,2CrO_4H_2$; and $Cr_2(SO_4)_3,3CrO_4H_2$, and are called the *chromosulphochromic acids*.[2]

The constitution of the green sulphate obtained by heating

[1] *Compt. rend.*, 1905, **140**, 42; **141**, 119, 331, 1024; 1906, **142**, 402; 1907, **144**, 79.

[2] Recoura, *Bull. Soc. chem.*, 1897, [3], **17**, 934.

the solid violet sulphate is at present unknown, but Recoura regards it as corresponding to the crystalline, green chloride described above, whilst Colson[1] has suggested that it is a condensed sulphate.

Sulphochromic Hydroxide, $[(SO_3)_4Cr_2O_2](OH)_2$.—When Recoura's green sulphate is treated with four, five, or six molecules of sulphuric acid, and the product heated for some time to 115°, transparent, vitreous products are obtained, having a bottle-green colour, much less distinct than that of the other green chromium derivatives. These dissolve in water, forming opaline solutions having a slight yellowish-green colour, which yield precipitates with all solutions of metallic salts, including those of the alkali metals. The solution of the product obtained by heating the green sulphate with four molecules of sulphuric acid gives, for example, a precipitate with potassium chloride having the composition $[(SO_3)_4Cr_2O_2](OK)_2$, and with cupric chloride one of the composition $[(SO_3)_4Cr_2O_2]O_2Cu$. In all these salts the metal is in combination with the chromium and not with the sulphuric acid, as on treatment with an excess of alkali they yield the chromites, the reaction with the copper salt being as follows:

$$[(SO_3)_4Cr_2O_2]O_2Cu + 8NaOH = 4Na_2SO_4 + Cr_2O_3,CuO + 4H_2O.$$

They are therefore termed the *sulphochromites.*[2]

Sulphochromic hydroxide itself has been prepared by heating the compound of chromic sulphate with four molecules of sulphuric acid to 140–150°; it is a grey, amorphous substance, is soluble in water, and has a heat of neutralisation higher than that of sulphuric acid (Recoura).[3]

Chromium and Nitrogen, Phosphorus, and Boron.

480 *Chromium Nitride,* NCr, is formed by the direct union of its elements at a red heat[4]; and also by passing ammonia over heated chromic chloride. It is a brownish-black powder, which takes fire and burns when heated to 200° in the air or in oxygen. Cold chlorine does not act upon it, but when heated in this gas small explosions first occur owing to formation of

[1] *Compt. rend.*, 1907, **144**, 206.
[2] Recoura, *Ann. Chim. Phys.*, 1895, [7], **4**, 516.
[3] See also Calvert and Ewan, *Proc. Chem. Soc.*, 1896, **12**, 160.
[4] Brieglieb and Geuther, *Annalen*, 1862, **123**, 239.

nitrogen chloride, and at last chromic chloride remains. It does not undergo change on ignition in hydrogen or in aqueous vapour, and is not attacked by caustic potash, hydrochloric acid, or nitric acid. Concentrated sulphuric acid converts it into the sulphates of ammonium and chromium :

$$2CrN + 4H_2SO_4 = Cr_2(SO_4)_3 + (NH_4)_2SO_4.$$

Chromic Nitrate, $Cr(NO_3)_3,9H_2O$, is obtained by dissolving the hydroxide in nitric acid, and crystallises in oblique, purple-red prisms. The solution, like that of the sulphate, turns green on boiling, and on evaporation dries to a green, amorphous mass. The green solution at once becomes violet on cooling.

Chromium Phosphide, PCr, is obtained by passing the vapour of phosphorus over ignited potassium chromate, or by heating chromic chloride with phosphorus in hydrogen.[1] On lixiviating the black fused mass with water, a grey, crystalline powder remains behind, having a metallic lustre, and possessing the above composition. It has the specific gravity of 5·71 (Maronneau),[2] and when heated in oxygen takes fire, and burns with formation of chromic phosphate.

Chromic Phosphates.—When a solution of sodium hydrogen phosphate is added to an excess of chrome alum a gelatinous precipitate is formed which on standing for 48 hours is transformed into dark-violet crystals of the phosphate[3] $CrPO_4,6H_2O$. A violet, non-crystalline compound of the same composition is obtained if an excess of sodium hydrogen phosphate is used. When dried at 100° it loses water and becomes green. A green phosphate probably identical with this product is obtained by the addition of an excess of the phosphate to chromic chloride solution; the composition of this is $CrPO_4,3H_2O$ according to Rammelsberg, or $2CrPO_4,5H_2O$ according to Bloxam, whilst Schiff states that the crystalline phosphate loses 3 molecules of water at 100°. A green compound, $CrPO_4,2H_2O$, is also obtained when the crystalline violet salt is treated with acetic anhydride (Schiff). If chromic hydroxide is dissolved in excess of phosphoric acid and the solution evaporated and heated to 316°, *chromic metaphosphate*, $Cr(PO_3)_3$, is obtained, which has been employed as a green pigment.

Chromium Borides.—Two chromium borides have been pre-

[1] Granger, *Compt. rend.*, 1897, **124**, 190.
[2] *Compt. rend.*, 1900, **130**, 656.
[3] Schiff, *Zeit. anorg. Chem.*, 1905, **43**, 304.

pared by heating the elements together in the electric furnace;[1] these have the formulæ CrB, and Cr_3B_2, and are grey crystalline substances.

Chromium and Carbon and Silicon.

481 *Chromium Carbides.*—When chromium is heated with an excess of carbon in the electric furnace the carbide, C_2Cr_3, is formed, which crystallises in brilliant plates having a fatty lustre, a specific gravity of 5·62, and a hardness intermediate between that of topaz and corundum. The crystals are not attacked by concentrated or dilute acids with the exception of dilute hydrochloric acid, which dissolves them slowly. Water has no action on it at 100°. A second carbide, CCr_4, is sometimes found on the ingots of metallic chromium prepared in the electric furnace, in needles 10–20 mm. long. These have a specific gravity of 6·75, and a hardness rather greater than that of quartz.[2]

Cyanogen Compounds of Chromium. Potassium Chromocyanide, $K_4[Cr(CN)_6],2H_2O$, is obtained by the action of potassium cyanide on chromous acetate, and forms blue crystals. It is soluble in water, and on exposure to air passes into the next compound.

Potassium Chromicyanide or *Potassium Hexacyano-chromite,* $K_3[Cr(CN)_6]$, forms light yellow, monoclinic crystals, obtained by pouring a solution of chromic acetate into a boiling solution of potassium cyanide.

A number of chromocyanides of other metals have also been prepared.[3]

Chromic Thiocyanate, $Cr(SCN)_3$.—Chromic hydroxide dissolves in thiocyanic acid, yielding a greenish-violet solution which when concentrated over sulphuric acid dries to a dark-green, amorphous, deliquescent mass. It forms a series of characteristic double salts, which are probably to be regarded as salts of a complex acid radical containing chromium.[4]

Potassium Chromithiocyanate or *Potassium Hexathiocyanochromite,* $K_3[Cr(SCN)_6],4H_2O$, is formed by heating a moderately

[1] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 16; Binet du Jassonneix, *Compt. rend.*, 1906, **143**, 897; Wedekind and Fetzer, *Ber.*, 1907, **40**, 297.

[2] Moissan, *Compt. rend.*, 1894, **119**, 185.

[3] Fischer and Benzian, *Chem. Zeit.*, 1902, **26**, 49; Cruser and Miller, *J. Amer. Chem. Soc.*, 1906, **28**, 1132.

[4] Rösler, *Annalen*, 1867, **141**, 185.

concentrated solution of 6 parts of potassium thiocyanate and 5 parts of chrome alum for 2 hours at the boiling point: the sulphates formed are precipitated by addition of alcohol, the filtrate evaporated and the residues recrystallised from alcohol. It forms tetragonal almost black crystals, which appear ruby-red by transmitted light, and dissolve very readily in water and alcohol, forming wine-red solutions. It is decomposed by alkalis and warm hydrochloric acid. The solution gives precipitates of analogous compounds with lead and silver salts.[1]

Chromium and Silicon.—Several silicides of chromium have been described: these are all prepared by heating chromium with silicon, or a mixture of silica and chromic acid with carbon or copper and aluminium in the electric furnace. In this way the compounds Si_2Cr, Si_2Cr_3, $SiCr_2$, and $SiCr_3$ have been obtained.[2] The compound, Si_2Cr_3, is also formed when silicon chloride is heated for some time in contact with chromium.[3]

Ammoniacal and Other Complex Compounds of Chromium.

482 The salts of chromium readily combine with ammonia or substituted ammonias to form complex salts. These contain for each atom of chromium, up to six molecules of ammonia and often other elements or groups of elements united with the metal to form a complex radical, which usually acts like a mono-, di-, or tri-valent metal, but may also have an acid function or be neutral. These complex salts are capable of undergoing numerous double decompositions, giving rise to a large number of derivatives, among which many cases of isomerism occur. Analogous compounds are formed by other metals, in particular, cobalt and the metals of the platinum group, and these are included in the following statement.

These compounds do not give the ordinary reactions of the metal, and in many cases this is also true of some or all of the acid radicals they contain. This is accounted for, as already explained (pp. 37–38), by supposing that in these latter cases, the acid radical forms part of the complex group containing

[1] Rösler, *Annalen*, 1867, **141**, 185.

[2] Moissan, *Compt. rend.*, 1895, **121**, 621; de Chalmot, *Amer. Chem. J.*, 1897, **19**, 69; Zettel, *Compt. rend.*, 1898, **126**, 833; Lebeau and Figueras, *ibid.*, 1903, **136**, 1329.

[3] Vigouroux, *Compt. rend.*, 1907, **144**, 83.

the metal, whereas those acid radicals which give the ordinary reactions are not contained in this group.

The constitution of these complex radicals is still under discussion, two different views being held. According to one of these (Blomstrand, Jörgensen) the metal retains its characteristic valency in all the compounds, the molecules of ammonia being attached to the metal in open chains by virtue of the pentavalent character of nitrogen. That portion of the acid radicals which does not retain its ordinary properties is directly connected with the metal, whilst the other portion is combined with nitrogen. Water may take the place of one or more of the ammonia groups, the oxygen atom being supposed to be tetravalent. The compound $Cr(NH_3)_5Cl_3$, in which only two of the chlorine atoms are precipitable by silver nitrate in aqueous solution, would thus receive such a constitutional formula as

$$\begin{matrix} & & Cl \\ & \diagup & \\ Cr & — & NH_3.NH_3.Cl \\ & \diagdown & \\ & & NH_3.NH_3.NH_3.Cl \end{matrix} .$$

The existence of isomerides may be readily expressed by a variation in the arrangement of the various groups.

The second view is that proposed by Werner,[1] who classifies these compounds on the theory of principal and supplementary valency, an account of which has already been given (p. 37), and which he has since modified in some few details. According to this theory, in the compound $[Cr(NH_3)_6]Cl_3$, for example, the ammonia groups are all united or *co-ordinated* with the chromium atom by means of its supplementary valencies, whilst the chlorine, according to Werner's more recent view, is combined with the complex radical as a whole, without being attached to any particular atom in it, and is said to be in *indirect combination* with this radical. The ammonia groups may be either partially or entirely replaced by acid groups such as Cl, NO_2, SCN, etc., yielding a large number of compounds, which always contain 6 groups in the complex radical. The valency of the complex radical is easily ascertained from the number and character

[1] *Annalen*, 1902, **322**, 261 ; *Neuere Anschauungen auf dem Gebiete der anorganische Chemie*, p. 58 (Vieweg and Sohn, *Braunschweig*, 1905). See also *Ber.*, 1907, **40**, 15, where a full account of the literature on the subject is given.

of the groups within it. If the number of monovalent acid radicals be less than the principal valency of the atom of the metal, the complex radical is basic and capable of combining with a number of acid radicals equal to the difference. If, however, it be greater, the complex radical has an acid character and is capable of combining with monovalent basic radicals equal in number to the excess of the number of monovalent acid radicals over the principal valency of the metal. When the number in the complex radical is equal to the principal valency of the metal, the compound is a neutral substance.

This is illustrated in the following series of compounds derived from trivalent chromium, X representing a monovalent acid, and R a monovalent basic radical:

$[Cr(NH_3)_6]X_3$ $[Cr(NH_3)_3(SCN)_3]$
$[Cr(NH_3)_5(SCN)]X_2$ $[Cr(NH_3)_2(SCN)_4]R$
$[Cr(NH_3)_4(SCN)_2]X$ $[Cr(NH_3)(SCN)_5]R_2$ (unknown)
$[Cr(SCN)_6]R_3$.

As already explained (p. 37), the electrolytic dissociation and the reactions of these compounds in solution correspond with these formulæ.

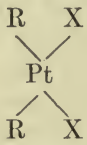
Compounds are also known, derived from the divalent atom of the metal, in which the complex radical contains six monovalent acid groups, and is therefore capable of uniting with four basic radicals, an example being potassium ferrocyanide, $[Fe^{II}(CN)_6]K_4$.

Cases of isomerism are known among these compounds, which depend on the position of the acid radicals within or without the complex radical, and such isomerides, from the fact that they dissociate differently in solution, are called *ionisation metamerides*. An example of this kind is found in the cobalt salts:

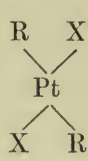
$$[Co(SO_4)(NH_3)_5]Br \text{ and } [CoBr(NH_3)_5]SO_4.$$

Isomerism may also be due to the geometrical arrangement of the co-ordinated groups around the central metal atom. In the case of the platinous compounds, in which only four groups are co-ordinated, these are accounted for by supposing that the radicals are arranged in one plane about the platinum atom. Isomerides are then possible only when the complex group has

the general formula PtR_2X_2, the possible cases being represented by the two following diagrams:



Asymmetric or Cis-form. (Platosemidiammine.)



Symmetric or Trans-form. (Platosammine).

In complex radicals of the type $[MeR_4X_2]$, the metal may be regarded as situated at the centre of a regular octahedron the corners of which are occupied by the co-ordinated groups. Two isomerides are then possible, the trans- or symmetrical form in which the groups X, X are situated at opposite ends of a diagonal of the figure, and the cis- or asymmetric form in which they are at adjacent corners. The compound $[CrCl_2En_2]X$, containing the divalent substituted ammonia ethylenediamine (En), forms two such isomerides. Many compounds are also known which are formed by the union of one or more basic complex radicals with one or more acid complex radicals. In this way isomerides may be obtained which differ in the complex radicals they contain, and these are known as *co-ordination isomerides*, as, for example, the compounds $[Cr(NH_3)_6].[Cr(SCN)_6]$ and $[Cr(NH_3)_4(SCN)_2].[Cr(NH_3)_2(SCN)_4]$. In a similar manner polymerides termed *co-ordination polymerides* may be formed, such as $[Cr(NH_3)_3(SCN)_3]$ and

$$[Cr(NH_3)_5(SCN)].[Cr(NH_3)_2(SCN)_4]_2.$$

Further, hydrated compounds exist, which may be regarded as ammoniacal compounds in which the ammonia groups in the complex radical are partially or entirely replaced by the group (OH_2). An example of this is seen in the following series of compounds:

$[Cr(NH_3)_6]Cl_3$; $[Cr(OH_2),(NH_3)_5]Cl_3$ &c. . . . $[Cr(OH_2)_6]Cl_3$,

the last compound being the violet or blue hexahydrated chromic chloride. In these compounds the chlorine may be made to pass into the complex radical, thereby replacing an (OH_2) group, thus:

$$[Cr(OH_2)(NH_3)_5]Cl_3 = [CrCl(NH_3)_5]Cl_2 + H_2O.$$

In a similar manner two (OH_2) groups in the complex radical of the violet chloride may be replaced by chlorine, yielding a

chloride which crystallises with two molecules of water to form the green hexahydrated chromic chloride, and this therefore has the constitution $[CrCl_2(OH_2)_4]Cl,2H_2O$.[1]

The third isomeric hexahydrated chromic chloride has been found to have the constitution $[CrCl(OH_2)_5]Cl_2,H_2O$. These facts are borne out by the manner in which the three chlorides are ionised in solution, and by their behaviour to silver nitrate.

The ammonia compounds are known as the *ammines*, this spelling of the word being adopted to avoid confusion with the organic *amines*, which have an entirely different constitution. The nomenclature of these compounds was originally founded on the colours characteristic of the various compounds, terms such as roseo-, praseo-, luteo-, croceo-, fusco-, xantho-, &c., having been employed. A much more rational proposal has been made by Werner, the principle of which is that the names of the various groups contained within the complex radical precede that of the metal, whereas those of the external group follow it, this being nothing more than an adaptation of the nomenclature frequently employed for organic compounds.

Thus the well-known cobalt compound $[Cl(NH_3)_5Co]Cl_2$, formerly known as purpureocobaltic chloride, receives the name chloro-pentammine-cobaltic dichloride, whilst the compound $[(OH_2)(NH_3)_5Co]Cl_3$ (roseocobaltic chloride) becomes aquo-pentammine-cobaltic trichloride, just as the organic compound $[C_6H_3Cl_2.CH_2]Cl$ is termed dichloro-benzyl chloride.[2]

Only a few examples of the chromammines are here described.[3]

Hexammine-chromium salts, $[Cr(NH_3)_6]X^I_3$, are prepared by the action of ammonia on many of the salts containing five molecules of ammonia.

Chloropentammine-chromium salts (purpureo-salts),

$$[CrCl(NH_3)_5]X^I_2.$$

[1] See also Bjerrum, *Ber.*, 1907, **40**, 2917.

[2] Some of the metals form more than one series of complex derivatives, corresponding to the different series of simple salts. In order to distinguish these compounds a special nomenclature has been introduced by Werner (*Neuere Anschauungen*, p. 73), according to which the valency of the metal is designated by the letters -a, -o, -i, -e, -an, -on, -in, -en for mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, and octo-valent elements respectively. Thus among the complex halogen derivatives of the platinum metals, the compound $K_2[PtCl_4]$ is known as potassium tetrachloroplatinoate, $K_3[RhCl_6]$ as potassium hexachlororhodiate, and $K_2[PtCl_6]$ as potassium hexachloroplatineate. This system has been adopted to some extent in Germany, but has not come into general use in England.

[3] A full account of the literature on this subject is given by Werner, *Ber.*, 1907, **40**, 15.

The chloride of this series together with *chloraquo-tetramminc-chromium chloride*, $[Cr(OH_2)Cl(NH_3)_4]Cl_2$, is formed by the action of liquid ammonia on violet chromic chloride. Other compounds of this class are the thiocyano-, nitrato-, and aquo-pentammine-chromium salts.

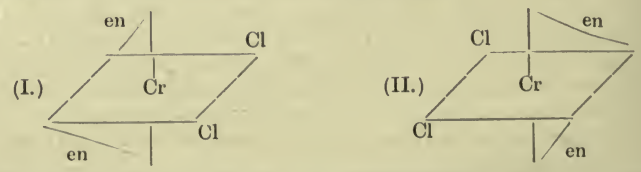
Trithiocyanotriammine-chromium, $[Cr(SCN)_3(NH_3)_3]$, is formed together with the tetrammine compound when the thiocyanate of the thiocyanopentammine compound is heated.

Tetrathiocyanodiammine-chromites, $[Cr(SCN)_4(NH_3)_2]R^I$.—When finely-divided potassium dichromate is added to fused ammonium thiocyanate ammonia is evolved, and the whole mass solidifies. When this is treated with water, filtered, and a few lumps of ammonium chloride added, scales of the salt $[Cr(SCN)_4(NH_3)_2]NH_4$ separate out.

This salt crystallises from solution on slow evaporation in dark-red, rhombic dodecahedra, which have the exact appearance of small garnets. When warmed with caustic potash these yield the corresponding *potassium* salt, $[Cr(SCN)_4(NH_3)_2]K$, which crystallises from water in lustrous, red scales. The free acid, $[Cr(SCN)_4(NH_3)_2]H$, is obtained by the action of sulphuretted hydrogen on the mercury salt and crystallises with one molecule of water in lustrous, red plates.

A number of compounds have been described which contain organic amines such as pyridine, ethylenediamine, &c., in the complex radical in place of ammonia.

Asymmetric Chromium Compounds.—The co-ordinated compounds of chromium show a close analogy with those of cobalt, and the discovery of optically active cobalt compounds pointed to the conclusion that if it were possible to obtain corresponding chromium compounds, these also should be capable of resolution into components which were optically active.[1] Werner has succeeded in preparing such a series, the 1 : 2-dichlorodiethylene-diaminechromic salts, $[Cl_2Cr\ en_2]X$, and has separated them into their optically active components. The two enantiomerides are represented by the configuration formulæ:



[1] Werner, *Ber.*, 1911, **44**, 3231.

(I) shows molecular asymmetry similar to that in the case of 1 : 2-dinitro- and of 1 : 2-dichloro-diethylenediaminecobaltic salts. Like the corresponding cobaltic salts the chromic salts are very unstable in aqueous solution. The active chromic salts show a much smaller rotatory power than the corresponding cobaltic compounds.

Detection and Estimation of Chromium.

483 Chromium oxide is frequently detected in its insoluble compounds by its characteristic green colour, as well as by the fact that it forms an emerald-green bead, both in the oxidising and reducing flames, with borax or microcosmic salt. On fusion with soda and saltpetre a yellow mass is obtained, which is soluble in water, and the solution acidified by acetic acid yields a yellow precipitate with soluble lead salts. Caustic potash or soda gives a green precipitate in solutions of chromic salts. This dissolves in an excess of alkali in the cold, but is completely precipitated on boiling the solution. This reaction is sometimes employed for the separation of chromium from aluminium, metals which are obtained together in the course of analysis. If, however, the solution contains large quantities of a zinc or magnesium salt, alkalis produce insoluble chromites of these metals, and these are precipitated in the following operations, together with iron. In this case the precipitate may be boiled with sodium hypochlorite or sodium peroxide, or fused with saltpetre and sodium carbonate, the fused mass dissolved in water, and the clear solution tested for a chromate. The detection of chromic acid is rendered easy by the bright yellow or red colour of its salts. The yellow colour of the normal chromates becomes red on the addition of an acid, and again yellow when made alkaline. Silver nitrate produces with the normal chromates a purple-red, and with the dichromates a dark-red precipitate, both being easily soluble in ammonia and in dilute nitric acid. Barium chloride gives a pale yellow precipitate with solutions of the normal chromates, and lead acetate throws down a pale yellow powder, insoluble in nitric acid, turned red by a slight excess of caustic potash, and soluble in a large excess of this reagent, and from this solution acetic acid again precipitates chrome-yellow. All the chromates are converted by reducing agents into the chromic salts. When they are distilled in the dry state with common salt and sulphuric acid, they yield

red vapours of chromyl chloride, which condense to a dark-red liquid, becoming yellow on saturation with ammonia.

The chromium salts do not impart any colour to the non-luminous gas flame. The spark spectrum of the metal is a complicated one, the brightest lines being 5208·8, 5207·4, 5204·7 in the green, and 4289·9, 4275·0, 4254·5 in the dark blue.

In order to estimate chromium gravimetrically in the chromium salts, a hot solution is precipitated with a small excess of ammonia, the solution boiled till the free ammonia is nearly all expelled, and the precipitate well washed with hot water, dried, ignited, and weighed as chromic oxide. In the chromates the chromium is either estimated by precipitating in acetic acid solution with lead acetate, and weighing the precipitated lead chromate ignited at a dull red heat, or the solution is mixed with hydrochloric acid and alcohol, or treated with sulphur dioxide, in order to form chromic chloride, which is then treated as above. Another good method is to precipitate the neutral solution, or one made slightly acid by nitric acid, with mercurous nitrate, and to convert the washed and dried precipitate by ignition into chromic oxide.

Soluble chromates may also be estimated volumetrically by determining the amount of a solution of a ferrous salt which a known quantity can convert into a ferric salt, the converse of this process, viz., the titration of a solution of a ferrous salt with standard potassium dichromate, being employed for the volumetric estimation of iron. A standard dichromate solution is also largely employed in other volumetric processes in which the reaction is one of oxidation.

For the valuation of chrome iron ore a large number of different methods have been proposed. The mineral is first fused with an alkali and oxidising agent, such as borax or sodium carbonate and nitre, or with sodium peroxide, in order to convert the chromium into a soluble chromate, which may be then estimated by the methods already mentioned. For details, works on analytical chemistry must be consulted.

Atomic Weight of Chromium.—The older atomic weight determinations gave varying results, owing to the inexact methods and impure material employed. Berlin[1] obtained the number 52·5 by the analysis of silver chromate, whilst Kessler obtained 52·3 from the determination of the equivalent

[1] *Annalen*, 1844, **56**, 207; 1845, **60**, 182.

quantities of potassium dichromate and potassium chlorate required to oxidise arsenious oxide to pentoxide.[1] Siewert[2] found 52·07 by the analysis of violet chromic chloride and of silver dichromate, and Baubigny[3] got 52·14 by the conversion of chromic sulphate into the trioxide. Rawson,[4] by the conversion of pure ammonium dichromate into chromium trioxide, found the value 52·15, and Meineke[5] obtained the average figure 52·12 by estimating (1) the quantity of silver and chromium in silver chromate and ammonio-silver chromate; (2) the quantity of oxygen in these two compounds; (3) the quantity of oxygen in potassium dichromate; and (4) the quantity of oxygen and of chromium in ammonium dichromate. More recently, Baxter and others,[6] by reducing silver chromate or dichromate with sulphurous acid or hydrazine sulphate, and then precipitating the silver as chloride or bromide, have found 51·995 for the atomic weight of chromium. The value now (1913) adopted is 52·0.

MOLYBDENUM. Mo = 96·0.

484 The name *Molybdæna*, which occurs in the writings of Dioscorides and Pliny, is derived from the Greek word μόλυβδος, lead, and was originally employed for the designation of a variety of substances containing lead. At a later time the name was used to signify galena or substances similar in appearance to this body, and to these the name of plumbago or black lead was also given. Even sulphide of antimony and pyrolusite, to which latter mineral Linnæus gave the name of molybdænum magnesii, were also classed among the same group of bodies. At a still later period this word was applied solely to graphite and to the mineral sulphide of molybdenum, which is extremely similar in its appearance to graphite.

The difference between plumbago and the sulphide of molybdenum was first pointed out by Scheele in his treatise on "Molybdæna" in 1778, and in another on "Plumbago" in 1779.[7] By heating the former mineral with nitric acid he

[1] *Pogg. Ann.*, 1861, **113**, 137.
[2] *Zeit. ges. Naturwiss.*, 1861, **17**, 530.
[3] *Compt. rend.*, 1884, **98**, 146.
[4] *Journ. Chem. Soc.*, 1889, **55**, 213.
[5] *Annalen*, 1891, **261**, 339.
[6] *J. Amer. Chem. Soc.*, 1909, **31**, 529, 541.
[7] *Vetensk. Acad. Handl.*

obtained sulphuric acid, together with a peculiar white earth which he recognised as an acid-forming oxide, and termed *acidum molybdænæ*, and he assumed that the mineral was a compound of this acid with sulphur. In 1781 Bergman suggested that the earth was probably a calx of a metal, and in 1782 he wrote that Hjelm had succeeded in preparing the metal, though the details of the experiments were first made known in 1790.

Another mineral containing molybdenum is the yellow molybdate of lead or wulfenite first found in Carinthia. This was investigated by the elder Jacquin, and he showed that it contained lead, but was doubtful as to the nature of the acid with which this metal was combined. Salzwedel, who analysed it in 1790, believed that it was a lead salt of tungstic acid, but Klaproth in 1797 ascertained its true composition. The compounds of molybdenum were then more accurately examined by Berzelius.

Molybdenum is usually found as molybdenite, MoS_2; also as wulfenite, $PbMoO_4$; it occurs more rarely as molybdic ochre, and pateraite, $CoMoO_4$. The former was for a long time believed to be molybdenum trioxide, MoO_3. Schaller,[1] however, from the analysis of a pure sample from Westmoreland, New Hampshire, has shown it to be a hydrated ferric molybdate, $Fe_2O_3,3MoO_3,7\frac{1}{2}H_2O$. Iron ores frequently contain traces of molybdenum, and hence this metal is also found in pig-iron as well as in the slag. Thus the iron slag obtained in the process of melting the cupreous schist at Mansfeld is said to contain from 9 to 28 per cent. of molybdenum.[2]

Metallurgy of Molybdenum.—Metallic molybdenum is obtained from its ores either by an electrical method or by reduction with aluminium.

By the electrical method, molybdenite is heated in a carbon tube with an arc of 350 ampères at 60 volts, when sulphur dioxide is evolved; the current is then increased to 900 ampères at 50 volts, when complete fusion takes place and the sulphur is entirely expelled. The metal prepared in this way, however, contains from 5 to 7 per cent. of carbon, which may be removed by heating with molybdic oxide. Molybdenum melts at $2450° \pm 30°$.[3]

A metal of 98 to 99 per cent., containing some iron and very

[1] *Amer. J. Sci.*, 1907, [iv.], **23**, 297.
[2] Heine, *J. pr. Chem.*, 1836, **9**, 177.
[3] von Pirani and Meyer, *Zeit. Elektrochem.*, 1912, **18**, 137.

small quantities of silicon, is obtained by the reduction of molybdic oxide by means of aluminium powder, as described under aluminium (p. 716).

Molybdenum is chiefly used in the form of rich ferro-molybdenum alloys for the manufacture of special steels.

Metallic molybdenum may be obtained on the small scale as a grey powder, which assumes a silver-white appearance under pressure, by heating the trioxide or one of the chlorides in a current of hydrogen, but is best prepared by heating a mixture of molybdenum dioxide with one-tenth of its weight of sugar charcoal in a carbon crucible in the electric furnace, the action of the arc being stopped before the portions in contact with the crucible have had time to fuse. It is thus obtained free from carbon, whereas if too strongly heated it takes up the latter in considerable quantities. The pure metal is as malleable as iron, and is not hard enough to scratch glass, has a specific gravity of 9·01, and can be forged when hot; it scarcely undergoes oxidation at the ordinary temperature, but is superficially attacked at a dull red heat, and rapidly at 600°, molybdenum trioxide subliming. It is rapidly attacked by fused potassium chlorate and nitrate. It may be distilled in the electric furnace, giving a vapour which solidifies in crystals.[1] When coarsely powdered it is attacked by fluorine at the ordinary temperature, by chlorine at a dull-red, and by bromine at a cherry-red heat, but not by iodine at the softening point of glass.

It is insoluble in dilute acids with the exception of nitric acid, but dissolves in concentrated sulphuric acid, the solution being first blue, but finally becoming colourless with formation of the trioxide, sulphur dioxide being also evolved. It is slowly attacked by fused alkalis.

Molybdenum forms amalgams which may be obtained by the electrical method. When these amalgams are distilled in vacuo, molybdenum is left behind in the pyrophoric state.[2]

[1] Moissan, *Compt. rend.*, 1906, **142**, 425.
[2] Férée, *Compt. rend.*, 1896, **122**, 733.

MOLYBDENUM COMPOUNDS.

Molybdenum and Oxygen.

485 Molybdenum combines with oxygen to form a series of oxides, many of which have a composition corresponding to those of chromium:

Molybdenum sesquioxide, Mo_2O_3,
Molybdenum dioxide, MoO_2,
Molybdenum trioxide, MoO_3.

The first two are basic oxides, but very little is known of their salts other than the halogen derivatives. The trioxide is the most important, and like the analogous chromium oxide is an acid-forming oxide giving rise to the important series of *molybdates*. A blue oxide, which is usually regarded as a combination of the dioxide with the trioxide, is also known, but its composition is not definitely settled, whilst an oxide, Mo_2O_5, and a peroxide have also been described.

The compound formerly described as a hydrated monoxide has been shown to be the hydroxide of molybdenum sesquioxide.

Molybdenum Sesquioxide, Mo_2O_3, is formed when one of the higher oxides is treated with sodium amalgam, zinc, &c. When the trioxide is thus treated, the colourless solution first becomes blue, then reddish-brown, and lastly black. The *hydroxide*, $Mo(OH)_3$, is obtained as a brownish-black powder by precipitating with ammonia, washing with dilute ammonia, and drying in a current of hydrogen at 100°. When gently ignited in absence of air the water is evolved, and the sesquioxide remains as a black mass (Berzelius). A black precipitate of this hydroxide is also produced when molybdenum dichloride is boiled with caustic potash, hydrogen being evolved during the reaction.[1] Molybdenum sesquioxide is insoluble in acids, and even the hydroxide dissolves only with difficulty.

The Salts of the Sesquioxide are black or of a dark purple colour in concentrated solution, but when diluted they are transparent and of a purple tint. In the solid form the sesquisalts are dark grey or black. They have a styptic taste, oxidise slightly on exposure to the air, are precipitated by alkalis with

[1] Muthmann and Nagel, *Ber.*, 1898, **31**, 2009.

formation of the hydroxide, and give a brown precipitate with ammonium sulphide soluble in excess of the reagent. Sulphuretted hydrogen also precipitates them, though slowly. Sodium phosphate produces a brownish-black precipitate.

Molybdenum Dioxide, MoO_2, is formed when the sesquioxide is gently heated in a current of air, or when sodium trimolybdate is ignited for several hours in a current of hydrogen. It is the only oxide formed when molybdenum trioxide is reduced by heating in hydrogen,[1] and may be prepared pure by heating this oxide first at 470° in a stream of the gas, and then in a current of dry hydrogen chloride, when any unchanged trioxide is converted into a volatile oxychloride and thus removed.[2] It is formed also when ammonium molybdate is fused with molybdenum trioxide,[3] and the product may be purified by washing successively with caustic soda, hydrochloric acid, and water, and then dried at 110°. The pure oxide is a brown or violet-brown, crystalline powder, and is reduced to the metal when heated at 600° in hydrogen. It is obtained in dark blue prisms resembling indigo by fusing sodium trimolybdate with one-third of its weight of zinc, and extracting the mass alternately with caustic potash and hydrochloric acid ;[4] this product, however, always contains a little admixed zinc molybdate, $Zn_2Mo_3O_8$, but it may be obtained pure by fusing together 8 grams of fused ammonium molybdate, 14 grams of potassium carbonate, and 7 grams of boron sesquioxide, and extracting the cooled melt with water. It then forms opaque tetragonal crystals, having a violet reflex, which are insoluble in boiling hydrochloric acid and caustic potash.[5]

Molybdic Tetrahydroxide, $Mo(OH)_4$, is obtained when a solution of the pentachloride or of ammonium molybdenum tetrachloride is precipitated with ammonia. On drying, the precipitate has a dark-red colour; it dissolves slowly in water, yielding a yellow or dark-red colloidal solution which reddens litmus, has a somewhat acrid and metallic taste, and is precipitated by the addition of salts. In closed vessels it decomposes after some time, forming a transparent jelly. The ignited dioxide does not dissolve in aqueous acids, although the hydroxide does so.

[1] Guichard, *Compt. rend.*, 1899, **129**, 722.
[2] Friedheim and Hoffmann, *Ber.*, 1902, **35**, 791.
[3] Guichard, *Compt. rend.*, 1899, **129**, 722; 1900, **131**, 998.
[4] Ullik, *Annalen*, 1867, **144**, 227.
[5] Muthmann, *Annalen*, 1887, **238**, 114.

The Salts of the Dioxide are very unstable, and are formed when an excess of molybdenum is treated with the corresponding acid, and then the requisite quantity of nitric acid added. The concentrated solutions are black, and on dilution they become of a bluish-green, greenish-yellow, dark-red, and lastly yellow colour. On exposure to the air they absorb oxygen and become blue, whilst with zinc they give a black precipitate of $Mo(OH)_3$. With alkalis they yield a reddish-brown precipitate, and with sulphuretted hydrogen and ammonium sulphide give the same reactions as the salts of the sesquioxide.

Molybdenum Trioxide and Molybdic Acid.

486 *Molybdenum Trioxide*, MoO_3, was supposed to occur as molybdic ochre, but this has been shown to be hydrated ferric molybdate. Gagarine[1] states, however, that he has found pure molybdic oxide as white or grey pseudomorphs after molybdenite in specimens from the Ilmen Mountains. It has a pearly lustre and is semi-transparent. It has probably been obtained by the oxidation of molybdenite which occurs there as pure sulphide without a trace of iron.

In order to prepare the trioxide in the pure state on the small scale the native sulphide may be heated in a combustion tube in a current of air until it is all oxidised, and the trioxide sublimed.[2] On the larger scale it may be obtained by mixing the same powdered mineral with an equal weight of pure quartz sand, and roasting the mixture on a flat iron plate. The roasted product is then boiled with dilute ammonia, and a small quantity of ammonium sulphide added to the solution in order to precipitate the copper. The filtered liquid is then evaporated to dryness, and the residue again dissolved in dilute ammonia. Crystals of ammonium molybdate are obtained from the filtrate on concentration. These are decomposed by nitric acid, evaporated to dryness, and the residual trioxide well washed with water. Molybdenum trioxide can also be obtained from native lead molybdate by first treating the mineral with dilute hydrochloric acid in order to remove iron, zinc, &c., then decomposing it with hot concentrated hydrochloric acid, evaporating down and digesting with dilute ammonia, when ammonium molybdate remains in solution and can be crystallised out as already

[1] *Bull. Acad. Sci. St. Petersbourg*, 1907, 287.

[2] Wöhler, *Annalen*, 1856, **100**, 376.

described.[1] The ammonium molybdate may also be converted into the trioxide by being ignited in a platinum dish and subsequently heated to a dull-red heat in a current of oxygen.[2]

Molybdenum trioxide is a white impalpable powder, which when heated becomes yellow; it melts at a red heat to a dark yellow liquid, which, on cooling, solidifies to a yellowish-white, fibrous, crystalline mass, having a specific gravity of 4·39 (Schafarik). It volatilises at very high temperatures when heated in closed vessels, but in the air it sublimes more easily, depositing small, colourless, transparent, rhombic tablets. It dissolves in 500 parts of cold, and in about 960 parts of hot water. The solution reddens litmus paper, turns turmeric paper brown, and possesses a sharp metallic taste.

Molybdic Acid, H_2MoO_4,H_2O or $MoO_3,2H_2O$, crystallises out in yellow crusts when three parts of ammonium molybdate are dissolved in twenty parts of water, the same quantity of nitric acid of specific gravity 1·16 added, and the whole allowed to stand. The deposition of the acid frequently takes place only very slowly, and the addition of a crystal of the compound renders its separation more easy.[3]

When the solution of the trioxide in nitric acid is allowed to evaporate spontaneously, a white, crystalline powder separates, which on heating loses water (Berzelius). This consists of the anhydrous acid, H_2MoO_4, which was once obtained by Ullik in the form of thin prismatic crystals by the decomposition of magnesium molybdate with nitric acid. It is also formed when the yellow acid is heated at 60°, or its solution in water concentrated at 40–50°, and is thus obtained in white needles which are very sparingly soluble in cold, but more readily in hot water.[4]

Colloidal Molybdic Acid.—When the hydrochloric acid solution of ammonium molybdate is dialysed, a yellow, strongly acid astringent solution of molybdic acid remains, which on evaporation yields a deliquescent, gummy mass.[5] After drying over sulphuric acid for several weeks it has the empirical formula $H_2Mo_2O_7$, but the determination of the molecular weight by

[1] Wöhler, *Mineralanalyse*, 146.

[2] Muthmann, *Annalen*, 1887, **238**, 117.

[3] Gmelin-Kraut, **2**, 171; Rosenheim and Bertheim, *Zeit. anorg. Chem.*, 1903, **34**, 427; 1906, **50**, 320; Graham, *Journ. Franklin Inst.*, 1907, **163**, 69.

[4] Rosenheim and Davidsohn, *Zeit. anorg. Chem.*, 1903, **37**, 314.

[5] Graham, *Journ. Chem. Soc.*, 1864, 326.

Raoult's method indicates that it contains four MoO_3 groups.[1] If ordinary ammonium molybdate is precipitated with barium chloride, and the washed precipitate decomposed with the exact quantity of sulphuric acid, a colourless solution is obtained, possessing an acid reaction and metallic taste. When dried over sulphuric acid for several months it has the composition $H_2Mo_2O_7$, and on heating at 100°, 120°, and 160–170°, the residues have the compositions $H_2Mo_2O_7$, $H_2Mo_4O_{13}$ and $H_2Mo_8O_{25}$ respectively; at 250° pure molybdenum trioxide remains behind.

Molybdenum trioxide generally behaves as an acid-forming oxide analogous to chromium trioxide, and unites with bases to form molybdates. The normal molybdates are unstable, and show a great tendency to form polymolybdates corresponding to the polychromates by uniting with further molecules of the trioxide, as many as ten molecules of MoO_3 combining with one equivalent of a basic oxide.

The molybdates also combine with other acidic oxides, forming the series of salts known under the general term of the complex molybdates. The best known of these are the phosphomolybdic acids, in which a varying number of molecules of molybdenum trioxide and of phosphoric anhydride are combined with a basic oxide (p. 1070); similar compounds are formed by the acidic oxides of arsenic, sulphur, vanadium, antimony, and also of iodine, tin, silicon, and manganese.[2] The exact constitution of these salts is not yet known.

Molybdenum trioxide acts towards strong acids as a basic oxide; thus it combines with two molecules of hydrochloric acid to form a volatile crystalline compound, which is probably the *hydroxychloride*, $MoO(OH)_2Cl_2$; with sulphuric acid it yields the compound[3] MoO_2SO_4, analogous to the salts formed by the trioxides of tungsten and uranium.

Sodium Molybdates.—The normal molybdate, Na_2MoO_4, is formed by fusing the trioxide with the requisite quantity of sodium carbonate, and crystallises from water in acute rhombohedra, containing two molecules of water; below 6° prisms containing 10 molecules of water separate out, resembling Glauber's

[1] Sabanéef, *Journ. Chem. Soc.*, 1890, **58**, 1215.

[2] Péchard, *Compt. rend.*, 1901, **132**, 628; Rosenheim and Itzig, *Zeit. anorg. Chem.*, 1898, **16**, 76; Friedheim and Samelon, *Zeit. anorg. Chem.*, 1900, **24**, 65; Rosenheim and Liebknecht, *Annalen*, 1899, **304**, 40; Asch, *Zeit. anorg. Chem.*, 1901, **28**, 273.

[3] Compare Guichard, *Compt. rend.*, 1906, **143**, 744.

salt in appearance; these effloresce in the air, forming the first-named salt. The *dimolybdate*, $Na_2Mo_2O_7$, is formed when sodium carbonate and the trioxide are fused in the requisite proportions, and is a crystalline mass soluble with difficulty in cold and only slowly in hot water. The *trimolybdate*, $Na_2Mo_3O_{10},7H_2O$, obtained in a similar manner, crystallises in large needles, 3·9 parts of which dissolve in 100 parts of water at 20°, and in 137 parts at 100°. The *tetramolybdate*, $Na_2Mo_4O_{13},11H_2O$, is prepared by the action of the calculated quantity of hydrochloric acid on the normal salt, and forms small, glistening crystals soluble with difficulty in cold, but readily in hot water. An excess of hydrochloric acid gives rise to the acid salt, $NaHMo_4O_{13}$, $8H_2O$, which forms long efflorescent monoclinic crystals readily soluble in water. *Sodium octomolybdate*, $Na_2Mo_8O_{25},4H_2O$, is formed as a white powder by the action of a solution of sodium carbonate on the acid salt, $HNaMo_8O_{25},4H_2O$, which latter salt is obtained by boiling the normal sodium molybdate with nitric acid, and also forms a white or yellowish powder. A sodium octomolybdate crystallising with $15H_2O$ has been obtained by the action of sulphur dioxide on a solution of the tetramolybdate.[1] The *decamolybdate*, $Na_2Mo_{10}O_{31},12H_2O$, is a white, crystalline powder obtained by heating the normal salt on the water-bath with sufficient hydrochloric acid to saturate the requisite quantity of sodium. It is sparingly soluble in water. If soluble molybdic acid be dissolved in the requisite quantity of sodium carbonate, the salt $Na_2Mo_{10}O_{31},21H_2O$ crystallises in monoclinic prisms; it is soluble in cold water without decomposition.

A salt containing 3 equivalents of soda to 7 of molybdenum trioxide is obtained by allowing a solution of the calculated quantity of the trioxide in sodium carbonate to evaporate spontaneously, the crystals having the composition $Na_6Mo_7O_{24},22H_2O$. On heating it loses water and yields the anhydrous salt, which solidifies in long needles readily soluble in water.

Potassium Molybdates.—The normal salt, K_2MoO_4, obtained in a similar manner to the sodium salt, crystallises in microscopic four-sided crystals, which are readily soluble in water. When hydrochloric acid is added drop by drop to a solution of the trioxide in potassium carbonate until a permanent turbidity is produced, a salt of the composition $K_6Mo_7O_{24},4H_2O$ separates

[1] Rosenheim, *Zeit. anorg. Chem.*, 1897, **15**, 180.

out on standing, in monoclinic prisms, which are decomposed by water into the *trimolybdate*, $K_2Mo_3O_{10},3H_2O$, which forms silky pliable needles. If this be dissolved in molybdic acid prepared from ammonium molybdate, a crystalline precipitate is formed which dissolves in hot water and on cooling deposits glistening crystals of the *tetramolybdate*, $K_2Mo_4O_{13},6H_2O$. A crystalline *octomolybdate*, $K_2Mo_8O_{25},13H_2O$, is also known (Rosenheim).

Ammonium Molybdates.—The *normal molybdate*, $(NH_4)_2MoO_4$, is produced when molybdenum trioxide or an ammonium polymolybdate is heated with excess of concentrated ammonia, and crystallises in four-sided prisms which are decomposed by water. When a solution of the trioxide in ammonia is evaporated, the compound $(NH_4)_6Mo_7O_{24},4H_2O$ (Delafontaine) crystallises out in large colourless monoclinic crystals. This is the salt usually known as ammonium molybdate. According to Klason,[1] however, the molecular weight in aqueous solution taking into account the degree of dissociation indicated by the electrical conductivity, shows that this salt is probably a double salt, $(NH_4)_3H_3Mo_3O_{12},(NH_4)_2H_4Mo_3O_{12}$, which is resolved into its constituents, triammonium and diammonium trimolybdates, when dissolved in water. On the other hand, Junius[2] gives the formula as $(NH_4)_{10}Mo_{12}O_{41}$. Results of physico-chemical measurements show that in aqueous solution the anion is $Mo_{12}O_{41}$, consequently this would appear to be the correct formula.[3] The *dimolybdate*, $(NH_4)_2Mo_2O_7$, separates out on evaporating the mother-liquor of the normal salt in the form of a white crystalline powder.[4] The *trimolybdate*, $(NH_4)_2Mo_3O_{10},H_2O$, is frequently formed by the decomposition of a solution of the ordinary salt at a low temperature, when it separates out in silky needles, sparingly soluble in cold, but readily so in hot water. Other crystalline ammonium salts have been described, which contain a larger proportion of molybdenum trioxide.[5]

Calcium Molybdate, $CaMoO_4$, is obtained by precipitating a solution of the ordinary ammonium salt containing an excess of ammonia with calcium chloride. It forms a white precipitate consisting of microscopic tetragonal pyramids. If calcium

[1] *Ber.*, 1901, **34**, 153.
[2] *Zeit. anorg. Chem.*, 1905, **46**, 428.
[3] Sand and Eisenlohr, *Zeit. anorg. Chem.*, 1907, **52**, 68.
[4] Compare Klason, *Ber.*, 1901, **34**, 153.
[5] Klason, *Ber.*, 1901, **34**, 153; Rosenheim, *Zeit. anorg. Chem.*, 1897, **15**, 180; 1903, **34**, 427; Mylius, *Ber.*, 1903, **36**, 638.

carbonate is boiled with an excess of the trioxide and water, and the solution allowed to evaporate spontaneously, *calcium trimolybdate*, $CaMo_3O_{10},6H_2O$, is deposited. The salt $H_2CaMo_8O_{26},17H_2O$ crystallises from a solution of the normal salt in the requisite quantity of hydrochloric acid. It is deposited in small oblique glistening prisms which are scarcely soluble in cold but readily dissolve in hot water.

Barium Molybdate, $BaMoO_4$, is a crystalline precipitate difficultly soluble in acids. It is obtained in tetragonal pyramids by fusing together sodium molybdate, barium chloride, and common salt.

When the ordinary ammonium salt is precipitated with barium chloride a flocculent precipitate of $Ba_3Mo_7O_{24},9H_2O$ is thrown down, which is slightly soluble in water. A compound, $BaMo_3O_{10},3H_2O$, having properties similar to the last salt, is obtained by precipitating a soluble trimolybdate. When barium carbonate is dissolved in soluble molybdic acid and the solution allowed to stand, oblique prisms of the salt $H_2BaMo_8O_{26},17H_2O$ are deposited; and if the normal salt be treated with dilute nitric acid the compound $BaMo_9O_{28},4H_2O$ is formed. This is insoluble in water and is not completely decomposed by acids, even by sulphuric acid.

Magnesium Molybdate, $MgMoO_4,5H_2O$, is obtained by boiling magnesia with water and molybdenum trioxide, and evaporating the solution, when the salt separates out in long glistening transparent prisms. Magnesium molybdate forms with the molybdates of potassium and sodium double salts such as $K_2MoO_4,MgMoO_4,2H_2O$, which appear to be isomorphous with the corresponding manganese and ferrous salts.

Lead Molybdate, $PbMoO_4$, occurs native as wulfenite in orange-red transparent tetragonal tablets and octahedra, which have a specific gravity varying from 6 to 7. When one part of sodium molybdate is fused with six parts of lead chloride and four of sodium chloride in a closed crucible, bright yellow translucent pyramids or tablets of the artificial compound are obtained, which have a specific gravity of 6·811. If a solution of a molybdate be added to one of lead nitrate the same compound is obtained in the form of a white precipitate which melts at a very high temperature. We are not acquainted with any other lead molybdate.

Molybdenum Molybdates.—When molybdic acid is reduced in solution by sulphuretted hydrogen, sulphur dioxide, stannous

chloride, etc., a blue solution is obtained, and this reaction forms one of the most characteristic tests for molybdenum. This is due to the formation of an oxide or oxides intermediate between the di- and the tri-oxide, and the solutions deposit a blue precipitate of this oxide which contains water and is termed *molybdenum blue*. It may also be obtained by adding a cold dilute hydrochloric acid solution of molybdenum dioxide to one of ammonium molybdate, and in several other ways. The solubility in water of the blue oxide varies with the conditions of precipitation.

Much doubt exists as to the composition of this substance; Rammelsberg assigned to it the formula $Mo_2O_5 = MoO_2,MoO_3$, and others have regarded it as $Mo_3O_8 = MoO_2,2MoO_3$, whilst according to Guichard[1] it has the composition $Mo_5O_{14},6H_2O = MoO_2,4MoO_3,6H_2O$. On the other hand, Klason[2] states that more than one compound exists, and regards these as complex derivatives of an oxide, Mo_2O_5, and molybdic acid, analogous to phosphomolybdic acid. Junius[3] has obtained it at the cathode by the electrolysis of molybdic acid in strong hydrochloric acid, and gives to it the formula, Mo_7O_{20}.

A brown hydroxide, $MoO(OH)_3 = Mo_2O_5,3H_2O$, is obtained according to Klason,[4] by treating ammonium molybdenum oxychloride, $MoOCl_3,2NH_4Cl$, with the exact amount of ammonia; on heating in carbon dioxide this loses water, and the oxide Mo_2O_5 is formed as a violet-black powder.

Several crystalline ammoniacal double molybdates have been described[5] of the general formula $M^I_2M^{II}(MoO_4)_2,2NH_3$, where $M^I = K$ or NH_4, and $M^{II} = Cu$, Zn, Cd, Ni, or Co.

487 *Phosphomolybdic Acid*, $H_3PO_4,12MoO_3$.—This complex acid is obtained by the repeated treatment of the ammonium salt with small quantities of aqua regia, and crystallises out on evaporation of the combined solutions. It forms at least three different crystalline hydrates, but the statements of different authors as to the number of molecules of water in these vary considerably. Debray[6] gives 21, 38, and 48 molecules to one of

[1] *Compt. rend.*, 1899, **129**, 722; Rogers and Mitchell, *J. Amer. Chem. Soc.*, 1900, **22**, 350; Junius, *Zeit. anorg. Chem.*, 1905, **46**, 426.

[2] *Ber.*, 1901, **34**, 148; see also Bailhache, *Compt. rend.*, 1901, **133**, 1210.

[3] *Zeit. anorg. Chem.*, 1905, **46**, 428.

[4] *Ber.*, 1901, **31**, 148; compare Guichard, *Compt. rend.*, 1902, **134**, 173.

[5] Briggs, *Journ. Chem. Soc.*, 1904, **85**, 672.

[6] *Compt. rend.*, 1868, **66**, 700.

P_2O_5, Gibbs[1] 27, 46, and 59 molecules, and Finkener[2] 29 and 58 molecules. Debray also believed the ratio $P_2O_5 : MoO_3$ to be 1 : 20, but Gibbs and Finkener have shown that it is 1 : 24.

Ammonium Phosphomolybdate, $(NH_4)_3PO_4,12MoO_3$.—This salt was discovered by Gmelin,[3] but Sonnenschein[4] was the first to notice that this compound contained phosphoric acid as an essential constituent. It is formed when a solution of a molybdate is mixed with ammonia, and a small quantity of phosphoric acid in nitric acid solution added, or when the free acid is added to a strongly acid solution of the ammonium salt. Under these circumstances a canary-yellow powder is thrown down. Pyro- and meta-phosphates do not yield this precipitate ; it is formed only when they are converted into orthophosphates, and when this change takes place slowly the compound is obtained in glistening yellow crystals (Debray). It is almost insoluble in water and in dilute acids and is also insoluble in a nitric acid solution of ammonium molybdate. The presence of hydrochloric acid and chlorides, as well as of many organic acids, with the exception of acetic acid, retards the formation, whilst in presence of an excess of phosphoric acid no precipitation occurs.

When dried above 130° it always has the composition given above, in which the ratio $P_2O_5 : MoO_3$ is 1 : 24, but according to Gibbs the hydrated precipitate has the composition $(NH_4)_3PO_4,12MoO_3,(NH_4)_2HPO_4,11MoO_3,8H_2O$. It dissolves in 10,000 parts of distilled water, in 6,600 parts of one per cent. nitric acid, and in 550 parts of hydrochloric acid of specific gravity 1·12. It is readily soluble in alkalis, and on allowing the ammoniacal solution to stand, glistening needles or prisms having the composition $2(NH_4)_3PO_4,5MoO_3,7H_2O$ separate out. These are sparingly soluble in cold, readily in hot water, forming a slightly acid liquid.

Phosphomolybdic acid also precipitates strongly acid solutions of the salts of rubidium, cæsium, thallium, and the organic alkaloids, but not solutions of sodium or lithium salts. The heavy metals are also not precipitated if a sufficient amount of free acid be present. This acid is used as a reagent for the alkaloids

[1] *Amer. Chem. J.*, 1881–2, **3**, 317.

[2] *Ber.*, 1878, **11**, 1638 ; see also Levi and Spelta, *Gazz.*, 1903, **33**, i., 207 ; Miolati, *ibid.*, ii., 335.

[3] *Handbook*, vol. iv., 68.

[4] *J. pr. Chem.*, **53**, 342.

or, in place of this, a liquid prepared by saturating a solution of sodium carbonate with molybdenum trioxide, and adding one part of sodium phosphate to every part of the trioxide, may be employed; this solution is evaporated to dryness, the residue fused, dissolved in water, filtered, and nitric acid added until the liquid becomes yellow.

In addition to these salts, others have been prepared in which the ratio $P_2O_5 : MoO_3$ is 1 : 15–18, and it appears not improbable that some exist in which the ratio is even higher than 1 : 24. Arsenic acid gives rise to an analogous series of complex acids, in the highest of which the ratio $As_2O_5 : MoO_3$ appears to be 1 : 20.

Permolybdic Acid.—The molybdates when treated with hydrogen peroxide in acid solution give a yellow coloration, but the yellow substance cannot be extracted with ether. If molybdenum trioxide be treated with hydrogen peroxide on the water-bath, and the mixture evaporated under diminished pressure, *permolybdic* or *ozomolybdic acid*,[1] H_2MoO_5,nH_2O, is obtained as an orange-red amorphous substance. Potassium trimolybdate dissolves in hydrogen peroxide yielding an orange-yellow solution, which on concentration at a moderate heat, yields yellow crystals of *potassium permolybdate*; this, according to Muthmann and Nagel,[2] has the composition $K_2O,2MoO_3,MoO_4,3H_2O$. These chemists have shown that the molybdates of the alkali metals, when dissolved in hydrogen peroxide, are able to take up additional oxygen to the extent of one atom or less per atom of molybdenum, and in this way they have prepared a number of *permolybdates* or *ozomolybdates*. These very readily lose their oxygen on heating.

A compound, K_2O_2,MoO_4,H_2O_2, is formed by the action of hydrogen peroxide at –12° on a solution of potassium permolybdate containing caustic potash. This is a brick-red mass which explodes spontaneously when preserved in quantity, and loses oxygen on exposure to the air, or on treatment with water.[3]

[1] Muthmann and Nagel, *Ber.*, 1898, **31**, 1836.

[2] *Zeit. anorg. Chem.*, 1898, **17**, 73; compare Péchard, *Compt rend.*, 1891, **112**, 720.

[3] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 632.

Molybdenum and the Halogens.

488 *Molybdenum Hexafluoride*, MoF_6, is obtained by passing dry fluorine over powdered molybdenum at 60–70°, the product being collected in a receiver cooled by a mixture of solid carbon dioxide and alcohol, and then purified by distillation. It is a snow-white crystalline substance, melting at 17° to a colourless liquid, which boils at 35°, and is decomposed by water with formation of a blue oxide.[1] It is not acted upon by chlorine, but reacts with arsenic trichloride and antimony pentachloride; it is reduced and turned blue by organic compounds.

Molybdenum Dichloride, $MoCl_2$, is prepared by heating the trichloride in a current of dry carbon dioxide:

$$2MoCl_3 = MoCl_2 + MoCl_4.$$

The tetrachloride volatilises, leaving the dichloride as a sulphur-yellow amorphous powder, which does not alter in the air, and does not dissolve in water but is soluble in alcohol and ether, separating from these solutions in the amorphous condition.[2] It is soluble also in the hydracids, in hot sulphuric acid, and in the alkalis. The hydrate, $MoCl_2,2H_2O$, crystallises from the hydrochloric acid solution, on standing, in pale-yellow plates insoluble in water, but when the solution is evaporated long prisms having the formula $MoCl_2,2H_2O$ are deposited. These are soluble in water, and when dissolved in hot hydrochloric acid long glittering needles of the compound $MoCl_2,3H_2O$, are deposited. These do not dissolve in water, but are decomposed by it with evolution of hydrochloric acid.

Molybdenum Dibromide, $MoBr_2$, is formed by the decomposition of the tribromide by heat. It forms a yellowish-red infusible mass which does not dissolve in water or in acids.

Molybdenum Di-iodide, MoI_2, is formed by heating the pentachloride in a current of hydrogen iodide. It is a brown amorphous substance of specific gravity 4·3, and is insoluble in water.[3]

The molecular formulæ of these compounds are probably treble those which are here given, for if the chloride be dissolved in caustic potash the compound $Mo_3Cl_4(OH)_2,2H_2O$ is thrown down on the addition of acetic acid in the form of a pale yellow

[1] Ruff and Eisner, *Ber.*, 1907, **40**, 2926.
[2] Liechti and Kempe, *Annalen*, 1873, **169**, 351.
[3] Guichard, *Compt. rend.*, 1896, **123**, 821.

amorphous precipitate. This compound, which has been termed *chloromolybdic hydroxide*, possesses basic properties, and forms well-defined salts with acids.[1] Moreover, the molecular weight [2] of the dichloride in alcohol corresponds to Mo_3Cl_6.

Chloromolybdic Bromide, $Mo_3Cl_4Br_2,3H_2O$, is obtained by heating the hydroxide or the chloride with hydrobromic acid. It crystallises on cooling in glittering reddish-yellow plates which scarcely dissolve in water or in dilute hydrochloric acid. If the mother-liquor of this salt be evaporated, well-formed, reddish-yellow prisms having the composition $Mo_3Cl_4Br_2,6H_2O$ are deposited. These dissolve in water, but are decomposed with separation of a yellow granular powder. Hydriodic acid forms corresponding compounds.

Bromomolybdic Hydroxide, $Mo_3Br_4(OH)_2,8H_2O$.—When molybdenum dibromide is dissolved in dilute alkali and the solution allowed to stand exposed to the air, or when ammonium chloride is added to the hot solution, the above compound is deposited in the form of golden-yellow glistening rhombohedra closely approximating in form to the cube. These lose six molecules of water on drying over sulphuric acid, and assume a dark-red colour. At 100° they lose all their water, a fine red powder remaining behind.[3]

Bromomolybdic Fluoride, $Mo_3Br_4F_2$, is prepared with hydrofluoric acid in the same way as the chloride, which it closely resembles.

Bromomolybdic Chloride, $Mo_3Br_4Cl_2,3H_2O$, is obtained as a pale-yellow powder on adding an excess of hydrochloric acid to the alkaline solution of the hydroxide.

Bromomolybdic Sulphate, $Mo_3Br_4SO_4,3H_2O$, can be obtained in the same way in the form of a yellow precipitate, whilst when the solution of the hydroxide is treated with ammonium molybdate and acetic acid, *bromomolybdic molybdate*, $Mo_3Br_4MoO_4,H_2O$, is thrown down as a reddish-yellow precipitate.

Molybdenum Trichloride, $MoCl_3$, is formed when the pure pentachloride is volatilised in a current of carbon dioxide, the tube being heated strongly at one point only. The trichloride is deposited as a copper-red crystalline crust.[4] If the pentachloride is heated in a current of hydrogen to 250° the trichloride

[1] Blomstrand, *J. pr. Chem.*, 1859, 77, 100.
[2] Muthmann and Nagel, *Ber.*, 1908, **31**, 2009.
[3] Atterberg, *Ber.*, 1873, **6**, 1464.
[4] Blomstrand, *J. pr. Chem.*, 1859, **77**, 96.

is obtained in a form closely resembling red phosphorus (Liechti and Kempe). Heated in the air it forms a white woolly sublimate, whilst impure dichloride remains behind. It is insoluble in cold water and is decomposed by boiling water. It likewise does not dissolve in hydrochloric acid, though it is easily soluble in hot nitric acid, whilst sulphuric acid dissolves it forming a blue solution which on heating becomes green. If the hydroxide is dissolved in hydrochloric acid a brown liquid is obtained which on evaporation dries to a black pitch-like mass.

Molybdenum Tribromide, $MoBr_3$, is formed by the action of bromine vapour on the heated metal. It sublimes as a mass of fine blackish-green needles which are insoluble in water though soluble in cold dilute nitric, and in boiling hydrochloric, acid. On boiling with alkalis the hydroxide is formed (Blomstrand).

Molybdenum Tetrachloride, $MoCl_4$, is obtained together with the dichloride, as has been stated, by heating the trichloride in an atmosphere of carbon dioxide. The tetrachloride volatilises as a dark yellow vapour which condenses to a brown crystalline powder. When exposed to the air it becomes of a bluish-green colour and deliquesces to a brown liquid. It is only slowly soluble in hydrochloric acid, and dissolves in concentrated sulphuric acid, giving a bluish-green colour.

Molybdenum Tetrabromide, $MoBr_4$, is formed in small quantities in the preparation of the tribromide as black glistening needles, which fuse when heated, volatilising in brownish-red vapours. These readily decompose into bromine and dibromide, and in presence of air the compound deliquesces, forming a dark liquid giving with more water a yellowish-brown solution.

Molybdenum Tetriodide, MoI_4.—The tetrahydroxide dissolves in hydriodic acid, giving a red-coloured solution; this on spontaneous evaporation yields crystals which transmit red light and appear brown by reflected light.

Molybdenum Pentachloride, $MoCl_5$.—This, the highest chloride of molybdenum, is formed by heating molybdenum or molybdenite in dry chlorine for some time, when bright metallic glistening black crystals are formed which melt at 194° and boil at 268°, giving a dark-red vapour with a specific gravity of 9·4–9·53,[1] corresponding to the above formula. The compound fumes on exposure to moist air and becomes coloured bluish-green, gradually deliquescing to a brown liquid which on dilution with water becomes colourless. Absolute alcohol and ether yield

[1] Debray, *Compt. rend.*, 1868, **66**, 732.

green solutions, and the chloride also dissolves in hydrochloric acid with evolution of heat. It is decomposed by water with formation of the tetrachloride, molybdic acid, and hydrochloric acid.[1]

When molybdenum trioxide is heated with phosphorus pentachloride to 170°, the compound $MoCl_5,POCl_3$ is formed. It crystallises in dark green prisms, and when further heated decomposes into its two constituents.

Oxy-Halide Derivatives of Molybdenum.

489 Molybdenum forms a large number of derivatives containing oxygen and the halogens, many of which are volatile and crystalline, and yield crystalline double salts with other metallic halides.

Molybdenyl Tetrafluoride, $MoOF_4$, is formed by the action of anhydrous liquid hydrofluoric acid on the corresponding oxychloride as a white hygroscopic body, melting at 97° and boiling at 180°.[2]

Molybdenum Dioxydifluoride, MoO_2F_2, is obtained by heating the trioxide with cryolite or lead fluoride as an amorphous sublimate having a bluish tinge, which decomposes in the air into hydrogen fluoride and molybdenum trioxide[3]; it is obtained in solution by dissolving the trioxide in hydrofluoric acid. It may also be obtained by the action of anhydrous liquid hydrofluoric acid on the dioxydichloride as a white, hygroscopic mass, which sublimes at about 270°, and turns blue in the air.[4] Crystalline double salts are formed by dissolving the normal and poly-molybdates in hydrofluoric acid.

Potassium Molybdenum Oxyfluoride, $K_2MoO_2F_4,H_2O = MoO_2F_2, 2KF,H_2O$, forms small triclinic crystals, and the salt $K_2(F_3MoO_2)_2,2H_2O = 2(MoO_2F_2,KF,H_2O)$ crystallises in silky needles which evolve hydrogen fluoride on exposure to air.[5] Double salts are also known of molybdenum oxytrifluoride and oxytetrafluoride with other fluorides.[6]

Molybdenyl Tetrachloride, $MoOCl_4$, is formed by the action of chlorine on a moderately-heated mixture of carbon and

[1] Guichard, *Bull. Soc. chim.*, 1901, [3], **25**, 188.
[2] Ruff and Eisner, *Ber.*, 1907, **40**, 2931.
[3] Schultze, *J. pr. Chem.*, 1880, **21**, 442.
[4] Ruff and Eisner, *Ber.*, 1907, **40**, 2933.
[5] Delafontaine, *Arch. Sc. Phys. Nat.*, 1855, **30**, 240.
[6] Marchetti, *Zeit. anorg. Chem.*, 1895, **10**, 66.

molybdenum dioxide. It forms a dark-green crystalline mass, or, if obtained at a higher temperature, light-green plates having a metallic lustre. It melts and evaporates below 100°, solidifying to a green glistening mass and yielding a dark-red vapour. It is readily decomposed by water, deliquescing in moist air to a blue liquid, and this on addition of water gives a blue precipitate which becomes brown in presence of ammonia. According to Klason,[1] this compound is molybdenyl trichloride, $MoOCl_3$, and not tetrachloride, since it yields with ammonia the double salt *ammonium molybdenyl chloride*, $MoOCl_3,2NH_4Cl$. The last compound may also be obtained by dissolving ammonium molybdate in fuming hydrochloric acid containing ammonium iodide and a small quantity of ammonium chloride, heating until no more iodine is set free, and saturating the cooled mixture with hydrogen chloride, when it separates in grass-green octahedra. Similar compounds have been obtained with potassium, rubidium, and cæsium chlorides.[2]

Molybdenum Dioxydichloride, MoO_2Cl_2.—This compound was originally supposed to be the hexachloride, its true composition being first ascertained by Rose. It is obtained by heating the dioxide in chlorine, and also, together with other chlorides, when a mixture of the trioxide and carbon is substituted for the dioxide. It sublimes usually as an amorphous mass, and melts only in closed vessels, in which it may be sublimed at low temperatures yielding thin tetragonal plates, or mossy aggregates. It dissolves readily in water and alcohol.

Dimolybdenum Trioxypentachloride, $Mo_2O_3Cl_5$, is frequently formed in the preparation of the molybdenum chlorides from materials containing oxygen, and is best obtained by heating the trioxide in chlorine; when carefully sublimed in a current of hydrogen it yields well-developed dark reddish-brown crystals; these may be readily melted and volatilised, and dissolve in water forming a solution which is first colourless, then green, and finally blue.

Another oxychloride, $Mo_2O_3Cl_6$, is obtained by the repeated sublimation of the oxytetrachloride, and forms well-developed violet prisms, which are decomposed on heating in the air into molybdenum dioxydichloride and chlorine. When heated to a temperature somewhat higher than that needed for its formation, it yields $Mo_3O_5Cl_8$, which forms pale-red needles

[1] *Ber.*, 1901, **34**, 148. [2] Nordenskjöld, *Ber.*, 1901, **34**, 1572.

and is stable in the air. Püttbach has prepared several other oxychlorides.[1]

Molybdenyl Dihydroxydichloride, $MoO(OH)_2Cl_2$, is obtained by the action of hydrogen chloride on the trioxide at 150–200°, and is a white crystalline substance which is volatile without decomposition only in an atmosphere of hydrogen chloride.[2]

A number of salts of chloromolybdic acids, which may be regarded as molybdates in which the oxygen and the hydroxyl groups are partially replaced by chlorine, have been described. The acid, $MoOCl_3.OH,7H_2O$, is obtained by the action of fuming hydrochloric acid on molybdenyl hydroxide, and a number of its salts have been prepared.[3]

Molybdenum Di-oxydibromide, MoO_2Br_2, is formed when bromine vapour is passed over the heated dioxide, or when a mixture of molybdenum trioxide and boron trioxide is heated with potassium bromide:

$$MoO_3 + B_2O_3 + 2KBr = MoO_2Br_2 + 2KBO_2.$$

It forms yellow tablets which deliquesce on exposure to air.

A number of bromomolybdates have been described (Weinland and Knöll).

Molybdenum and Sulphur.

490 *Molybdenum Sesquisulphide,* Mo_2S_3, is obtained when the disulphide is heated in the electric furnace. It forms steel-grey needles of specific gravity 5·9 at 15°, and is converted into metallic molybdenum when heated to a higher temperature than that at which it is formed.[4]

Molybdenum Disulphide, MoS_2, is found native as molybdenite in Sweden, Norway, Bohemia, Saxony, the Urals, at Caldbeck Fells in Cumberland, in Connecticut, California, and elsewhere. It commonly occurs in foliated masses or in scales, and sometimes in tabular hexagonal prisms, and in its general appearance is very similar to graphite, since it possesses a metallic lustre and pure lead-grey colour, and leaves a grey trace on paper. Molybdenite generally occurs embedded in or disseminated through granite, gneiss, zirconsyenite, granular limestone, and other crystalline rocks.

[1] *Annalen*, 1880, **201**, 123. [2] Debray, *Compt. rend.*, 1858, **46**, 1101.
[3] Weinland and Knöll, *Ber.*, 1904, **37**, 569; *Zeit. anorg. Chem.*, 1905, **44**, 81.
[4] Guichard, *Bull. Soc. chim.*, 1900, [3], **23**, 147.

When the trioxide is fused with sulphur, or heated in a current of sulphuretted hydrogen, the same compound is obtained in the form of a glistening black powder, easily distinguished from graphite by the facts that when heated before the blowpipe it is incombustible, that it oxidises when heated in the air with evolution of sulphur dioxide and formation of molybdenum trioxide, and that it is readily oxidised by nitric acid and aqua regia.

Molybdenum Trisulphide, MoS_3, is formed when sulphuretted hydrogen is passed into the concentrated solution of a molybdate and hydrochloric acid added to the liquid. It may likewise be prepared by boiling the molybdate of an alkali metal for a short time with ammonium sulphide, and then precipitating with dilute sulphuric acid. Thus obtained it is a reddish-brown precipitate which dries to a blackish-brown powder. On heating in absence of air it splits up into the foregoing compound and sulphur. It combines with basic sulphides to form soluble thio-salts.

Potassium Thiomolybdate, K_2MoS_4, is formed when potassium molybdate is saturated with sulphuretted hydrogen. On evaporating the solution the compound crystallises out in ruby-red four- or eight-sided tablets which have a green metallic lustre, and dissolve in water to form a yellowish-red solution.

Ammonium Thiomolybdate, $(NH_4)_2MoS_4$, is obtained by dissolving the trisulphide in ammonium sulphide, and crystallises in cinnabar-red scales.

A series of complicated mono- and di-thiomolybdates has been described by Krüss.

Molybdenum Tetrasulphide, MoS_4, is obtained by heating pentathiomolybdic acid to 140° as a cinnamon-brown powder which undergoes slight oxidation in the air. The pentathio-acid is obtained as a reddish-brown powder by the action of dilute hydrochloric acid on the potassium salt.

Potassium Pentathiomolybdate, $KHMoS_5$, is obtained by evaporating a solution of potassium dimolybdate which has been saturated with sulphuretted hydrogen, and separates in blood-red prisms probably belonging to the rhombic system, which are sparingly soluble in water. A black powder consisting of molybdenum di- and tri-sulphides separates out at the same time.[1]

Perthiomolybdic Acid, $HMoS_6$.—When a solution of normal

[1] *Annalen*, 1884, **225**, 1.

ammonium thiomolybdate is mixed with a solution of ammonium polysulphides, *ammonium hexathiomolybdate* or *perthiomolybdate* separates out in black lustrous needles, which are sparingly soluble in water and alcohol. By the action of caustic potash it yields the corresponding potassium salt, $KMoS_6$, which crystallises in thin dark-brown plates, and is more soluble in water than the ammonium salt. The free acid, $HMoS_6$, is obtained by treating the ammonium salt with cold 10 per cent. hydrochloric acid and washing the product with carbon disulphide.[1]

Molybdenum and Nitrogen, Phosphorus, Boron, Carbon, and Silicon.

491 *Molybdenum Nitride.* — When molybdenum oxide, hydroxide, or mixtures of the two are heated to 500–600° with equal parts of nitrogen and hydrogen under a pressure of about 60 atmospheres a molybdenum nitride is formed. It is used technically and when heated in a vacuum yields pure metallic molybdenum and ammonia.[2]

Molybdenum Phosphide, MoP, is obtained by strongly heating molybdenum trioxide and metaphosphoric acid in a carbon crucible. It forms a grey vesicular mass having a metallic lustre and containing crystals in the cavities. On ignition in the air it oxidises slowly, and it takes fire when thrown into fused nitre.

Molybdenum Boride, Mo_3B_4, is formed when the elements are heated together in the electric furnace [3] as a pale brass-like substance of the specific gravity 7·105.

Molybdenum Carbides.—The carbide, MoC, is obtained by fusing in the electric furnace [4] a mixture of molybdenum, carbon, and aluminium, as a grey crystalline powder of specific gravity 8·40 at 20°, whilst the compound, Mo_2C, is formed when calcium carbide is heated in the electric furnace with molybdenum dioxide.[5]

Molybdenum Silicide, Mo_2Si_3, is formed as a crystalline compound when the oxide obtained by calcining ammonium molybdate is heated with silicon in the electric furnace.[6]

[1] Hofmann, *Zeit. anorg. Chem.*, 1896, **12**, 55. [2] D. R. P., 246554.
[3] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 16.
[4] Moissan and Hoffmann, *Compt. rend.*, 1904, **138**, 1558.
[5] Moissan, *Compt. rend.*, 1897, **125**, 839.
[6] Vigouroux, *Compt. rend.*, 1899, **129**, 1238.

Detection and Estimation of Molybdenum.

492 Molybdenum trioxide and the molybdates may be detected inasmuch as the colourless hydrochloric acid solution when brought into contact with zinc becomes of a blue, green, and lastly dark-brown colour. The lower oxides, as well as their salts, can be readily transformed into the molybdates by oxidation. Molybdenum trioxide colours the blowpipe flame a yellowish-green, and imparts to a bead of borax or microcosmic salt a fine green colour in the reducing flame. Hydrochloric or nitric acid produces a curdy precipitate in solutions of a molybdate when not too dilute. This dissolves in an excess of acid, and even in a large quantity of water. A solution of ammonium molybdate in nitric acid becomes yellow-coloured on the addition of a few drops of sodium phosphate, and on warming a heavy yellow precipitate of ammonium phosphomolybdate (p. 1071) separates out. If some zinc be added even to a very dilute solution of a molybdate, and then hydrochloric acid and a concentrated solution of potassium thiocyanate, the liquid becomes coloured deep red, the red compound being extracted on shaking up with ether. The ethereal solution is first orange-red, but becomes carmine-red by the oxidising action of the air.

Molybdenum trisulphide is slowly precipitated from an acid solution by sulphuretted hydrogen, and it dissolves readily in ammonium sulphide. When the solution containing ammonium thiomolybdate is acidified with dilute nitric acid, molybdenum trisulphide is thrown down.

In order to estimate molybdenum *quantitatively* it must be obtained as a neutral molybdate, which is then precipitated with a neutral solution of mercurous nitrate. The yellow precipitate which falls down is washed with a solution of mercurous nitrate, dried, and then either heated in a stream of hydrogen, when molybdenum dioxide is formed, or ignited with a weighed quantity of anhydrous lead oxide until all the mercury is driven off. The increase of weight then gives the amount of trioxide present.

It can be estimated also volumetrically. In acid solutions molybdic salts are reduced by zinc to the sesqui-compounds, which can then be titrated with standard permanganate:

$$5M_2O_3 + 6KMnO_4 + 9H_2SO_4 = 10MoO_3 + 6MnSO_4 + 3K_2SO_4 + 9H_2O.$$

Atomic Weight of Molybdenum.—The determination of the atomic weight of molybdenum has been frequently made, but with varying results. After an inaccurate determination by Berzelius, Svanberg and Struve obtained the number 92·5, which was confirmed by Berlin, and then generally adopted. The investigation of Dumas[1] then showed that the number just quoted was distinctly too low, the average obtained by the reduction of the trioxide to the metal in a current of hydrogen being 95·9; the numbers in the different experiments varying, however, from 95·3 to 96·2. Debray[2] obtained the number 95·5 by the same method, whilst Liechti and Kempe[3] by the analysis of the di-, tri-, and penta-chloride of molybdenum obtained the same average number as Dumas; but in this case also the numbers found in the different experiments varied considerably. More recently Smith and Maas[4] have found the number 96·06, the method adopted being to heat pure sodium molybdate in a current of hydrogen chloride, when the following reaction takes place:

$$Na_2MoO_4 + 4HCl = 2NaCl + Mo(OH)_2OCl_2 + H_2O.$$

The last two being volatile, only pure sodium chloride remains behind, and from the amount of this obtained from a given quantity of sodium molybdate, the above number was obtained as the average of ten closely agreeing experiments. Lastly, Seubert and Pollard,[5] by the acidimetric determination of molybdic acid, obtained the number 95·92, and by the reduction of the trioxide to the metal in a current of hydrogen the number 96·01. The atomic weight now adopted (1913) is 96·0.

TUNGSTEN. W = 184·0.

493 The minerals tungsten or heavy-stone, now termed scheelite or calcium tungstate, and wolfram (the *lupi spuma* of Agricola) were, up to the middle of the eighteenth century, both classed amongst the tin ores. In 1781, Scheele proved that tungsten was composed of lime combined with a peculiar acid, and in the same year, Bergmann stated that, in his opinion, this

[1] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.
[2] *Compt. rend.*, 1868, **66**, 732.
[3] *Annalen*, 1873, **169**, 360.
[4] *Zeit. anorg. Chem.*, 1893, **5**, 280.
[5] *Zeit. anorg. Chem.*, 1895, **8**, 434.

acid was a metallic calx. Two years later the Spanish chemists Juan, José, and Fausto d'Elhujar,[1] showed that this same acid is contained in the mineral wolfram, combined with iron and manganese. They succeeded also in producing metallic tungsten from the acid.

Tungsten is not a common metal, being found only in a few minerals, some of which occur, however, in fairly large quantities. The most important of these is wolfram, or wolframite, a tungstate of iron and manganese, $(Fe,Mn)WO_4$, found in Cornwall, in Cumberland, on Rona in the Hebrides, in County Wicklow, at Zinnwald, in many localities in the United States, and also in Austria-Hungary, Spain, Portugal, Queensland, New Zealand, Tasmania, Canada, and various parts of South America. Other important tungsten minerals are scheelite or calcium tungstate, $CaWO_4$, and stolzite or lead tungstate, $PbWO_4$. In addition to these, tungsten occurs in the following somewhat rare minerals: wolframochre, WO_3; ferberite, $2(Fe,Mn)WO_4,(Fe,Mn)O$; hübnerite, $MnWO_4$; and cuproscheelite, or cuprotungstite, $(Ca,Cu)WO_4$.

Metallic Tungsten is obtained from wolfram by a method which consists of three distinct stages.[2] Sodium tungstate is first prepared by heating together a mixture of the ground ore and sodium carbonate. When this operation is carried out under proper conditions the extraction is complete, and at the same time any tin and silica present are left insoluble. The sodium tungstate thus formed is dissolved in water and separated from the oxides of iron, aluminium, manganese, tin, and silicon, by filtration, and tungstic acid, H_2WO_4, is then precipitated by means of acid. In this step care is necessary to prevent the formation of hydrated tungstic acid, which is soluble (see p. 1087). The tungstic acid thus obtained is washed free from soda salts and dried, and the resulting tungstic oxide is mixed with carbonaceous materials and submitted to a high temperature in crucibles for reduction to metal. A well-fired crucible when opened should be uniform throughout, with the exception of a thin layer of tops or undecomposed tungstic oxide and carbon, which can be readily removed.

[1] *A Chemical Analysis of Wolfram and Examination of a New Metal, which enters into its Composition.* Translated from the Spanish by C. Cullen, to which is prefixed a translation of Mr. Scheele's analysis of the Tungsten, or heavy-stone, with Mr. Bergmann's supplemental remarks. London, 1785.

[2] Hadfield, *J. Iron Steel Institute*, 1903, **64**, 38.

Tungsten containing 99 per cent. of the metal has been obtained by fusing tungsten trisulphide with lime.[1]

Metallic tungsten is generally used in commerce in the powdered state, but a considerable quantity of ferrotungsten is manufactured by means of the electric furnace, and alloys with manganese and other metals can be obtained by reducing a mixture of the oxides with aluminium. The purest forms of tungsten at present obtainable are hard and brittle, and are not ductile either at ordinary temperatures or when heated.

Metallic tungsten may be prepared on the small scale by the reduction of the trioxide with carbon or in a current of hydrogen, by the reduction of the chloride in sodium vapour, or by heating a mixture of the trioxide with one-tenth of its weight of sugar charcoal in the electric furnace; if care be taken that complete fusion of the metal does not occur, the latter is free from carbon.[2] The metal thus obtained is as a rule fused on the surface, but is porous internally, and can be welded like iron. It has been obtained in the form of a regulus by reducing the oxide with aluminium turnings and at the close of the reaction adding aluminium foil, and blowing in a stream of oxygen, or by adding liquid air to a mixture of the oxide and aluminium and igniting as in the thermite process.[3] The powdered metal can be prepared also by heating the oxide with zinc and extracting the product with caustic soda solution,[4] and by the action of dilute acids on the alloys of manganese and tungsten.[5]

In the form of a regulus tungsten has a slightly darker colour than zinc, shows a crystalline structure, is harder than glass, and has the sp. gr. 16·6 (Stavenhagen), whereas the metal obtained by Moissan did not scratch glass, and had a sp. gr. of 18·7.[6] The metal is not magnetic, it has the specific heat 0·0340 at 93°, 0·0375 at 423°,[7] melts [8] at about 2,800°, and can be volatilised in the electric furnace, but is more refractory than iron, molybdenum, or uranium.[9] Von Pirani and Meyer [10]

[1] Weiss, *Zeit. anorg. Chem.*, 1910, **65**, 279.
[2] Moissan, *Compt. rend.*, 1896, **123**, 13.
[3] Stavenhagen, *Ber.*, 1899, **32**, 1513, 3064.
[4] Delépine, *Compt. rend.*, 1900, **131**, 184.
[5] Arrivant, *Compt. rend.*, 1906, **143**, 594.
[6] See also Roscoe, *Mem. Manch. Phil. Soc.*, 1872, [3], **5**, 77.
[7] Defacqz and Guichard, *Ann. Chim. Phys.*, 1901, [7], **24**, 139.
[8] Wartenberg, *Ber.*, 1907, **40**, 3287.
[9] Moissan, *Compt. rend.*, 1906, **142**, 425.
[10] *Ber. deut. physikal. Ges.*, 1912, **14**, 426.

give the melting point at 3100°±60°. It is attacked by fluorine at the ordinary temperature with incandescence, and by chlorine at 250–300°, but has no action on nitrogen and phosphorus at a red heat; when heated with carbon, silicon, or boron in the electric furnace it yields crystalline compounds having a metallic lustre, which are hard enough to scratch rubies. It is slowly attacked by fuming sulphuric acid and by fused alkalis.[1] At a red heat the powdered metal burns in air forming the trioxide, but it is not readily oxidised by moist air although slowly attacked by water containing carbon dioxide; it is readily oxidised when heated with oxidising agents such as lead dioxide or potassium chlorate. Sulphuric, hydrochloric, and hydrofluoric acids act upon it slowly, but it is readily dissolved by a mixture of nitric and hydrofluoric acids; the powdered metal is rapidly oxidised by aqua regia, and dissolves in boiling caustic potash solution with formation of potassium tungstate and evolution of hydrogen, whereas the fused metal is not attacked by aqua regia, but dissolves slowly in fused potash (Stavenhagen). Tungsten has been utilised for the production of filaments for incandescent electric lamps which have a very high efficiency.[2] It is also largely employed in the manufacture of tungsten steels, generally in the form of ferro-tungsten.

COMPOUNDS OF TUNGSTEN.

Tungsten and Oxygen.

494 Tungsten forms two definite oxides: tungsten dioxide, WO_2, and tungsten trioxide, WO_3. These combine together to form compounds analogous to the blue oxides of molybdenum (p. 1081).

Tungsten Dioxide, WO_2.—This oxide is formed when a current of hydrogen is passed over the trioxide, WO_3, at a dull red heat. It may also be obtained in the wet way by reducing the trioxide, mixed with hydrochloric acid, by means of metallic zinc, or by the action of water on the tetrachloride. In preparing it in the dry way care is needed, as if the temperature be too high metallic tungsten is formed, whereas if the heat be not sufficient, the intermediate blue oxide is produced. Tungsten

[1] Ruder, *J. Amer. Chem. Soc.*, 1912, **34**, 387.

[2] *J. für Gasbeleuchtung*, 1906, **49**, 756; *Nature*, 1907, **76**, 156; *J. Inst. Elect. Engineers*, 1907, **38**, 211.

dioxide is a brown powder of specific gravity 12·1, which has a copper-red colour when crystalline trioxide is employed for its preparation. It is strongly pyrophoric, and must be cooled in hydrogen for some time before it is exposed to the air. It is slightly soluble in concentrated hydrochloric acid and sulphuric acid, yielding purple solutions. Oxidising agents convert it rapidly into the trioxide. It dissolves in potash with disengagement of hydrogen and the production of potassium tungstate:

$$WO_2 + 2KOH = K_2WO_4 + H_2.$$

Tungsten Trioxide, WO_3.—This oxide occurs native as wolframine, a yellow powder found together with other tungsten minerals in Cumberland, near Limoges, in Connecticut, and in North Carolina. In order to prepare the trioxide, the method already described (p. 1083) may be adopted, or finely powdered wolfram may be digested for a long time with hydrochloric acid, the mixture frequently shaken, the acid renewed, and a little nitric acid added towards the end of the process to oxidise the iron. This is continued until the acid has dissolved out the whole of the iron and manganese and the brown powder has become yellow-coloured. The insoluble portion consisting of tungsten trioxide and undecomposed wolfram and quartz, after being well washed, is shaken up with a solution of ammonia which dissolves the liberated tungstic acid. The solution is crystallised and the crystals are converted into the trioxide by ignition in the air. Wöhler converted the wolframite into calcium tungstate by fusing the finely powdered mineral for an hour with twice its weight of chloride of calcium and then lixiviating, when calcium tungstate remained behind. This was then decomposed by nitric acid, and tungsten trioxide obtained by igniting the yellow precipitate thus thrown down. The native tungstate of calcium (scheelite) can also be decomposed in this way.

Tungsten trioxide is a bright canary-yellow coloured amorphous powder which becomes dark-orange on heating, but regains its bright yellow colour on cooling. A very slight admixture of sodium salt imparts to the oxide a greenish tint which no amount of oxidation can remove (Roscoe). It also becomes greenish on exposure to light. Tungsten trioxide has been obtained in the crystalline state by Debray, by igniting a mixture of sodium tungstate and carbonate in a current

of hydrochloric acid, when the trioxide is obtained in olive-green rectangular prisms which sublime at a white heat. The crystalline trioxide has also been prepared by heating hydrated tungstic acid with borax in a porcelain tube (Nordenskjöld). The specific gravity of tungsten trioxide thus obtained is 6·34. The amorphous oxide is soluble and the crystalline oxide insoluble in sulphur monochloride.[1]

Tungstic Acid and the Tungstates.

495 Tungsten trioxide is an acid-forming oxide, and yields two tungstic acids, the normal acid, H_2WO_4, and metatungstic or tetratungstic acid, $H_2W_4O_{13}$, the salts of which correspond to the tetrachromates and tetramolybdates. In addition to the salts corresponding to these acids, a large number of other tungstates analogous to the polychromates and polymolybdates have been prepared, the formulæ of which are given in the following columns:[2]

$M^I_2WO_4 = M^I_2O,WO_3$.	$M^I_2W_8O_{25} = M^I_2O,8WO_3$.
$M^I_2W_2O_7 = M^I_2O,2WO_3$.	$M^I_4W_5O_{17} = 2M^I_2O,5WO_3$.
$M^I_2W_3O_{10} = M^I_2O,3WO_3$.	$M^I_6W_7O_{24} = 3M^I_2O,7WO_3$.
$M^I_2W_4O_{13} = M^I_2O,4WO_3$.	$M^I_8W_3O_{13} = 4M^I_2O,3WO_3$.
$M^I_2W_5O_{16} = M^I_2O,5WO_3$.	$M^I_{10}W_{12}O_{41} = 5M^I_2O,12WO_3$.
$M^I_2W_6O_{19} = M^I_2O,6WO_3$.	

Many of these crystallise with a number of molecules of water, forming well-developed crystals. The salts of the formula $M^I_{10}W_{12}O_{41}$ are termed paratungstates.

The tungstates also yield complex salts with many other acidic oxides analogous to the complex molybdates.

Tungstic Acid, H_2WO_4.—When a solution of a tungstate is precipitated by an acid in the cold, a white precipitate is thrown down consisting of hydrated tungstic acid, H_2WO_4,H_2O. This is soluble in water, possesses a bitter taste and reddens litmus. If, on the other hand, an excess of hot acid be used, anhydrous tungstic acid, H_2WO_4, separates as a yellow powder, insoluble in water and in all acids except hydrofluoric acid. If pure tungsten hexachloride be exposed to the action of moist air, the red

[1] Smith and Fleck, *J. Amer. Chem. Soc.*, 1899, **21**, 1008.

[2] See Schaefer, *Zeit. anorg. Chem.*, 1904, **38**, 142, where the literature is quoted.

monoxychloride is first formed, and this soon passes into a fine flocculent mass of tungstic acid.

The tungstates are insoluble in water with the exception of those of the alkali metals; and even of these, some tungstates of potassium and ammonium are only sparingly soluble. The tungstates of the alkaline earth metals, and of the heavy metals are mostly amorphous powders, but they may be obtained in the crystalline state by double decomposition at a high temperature.

Metatungstic Acid, $H_2W_4O_{13},7H_2O$.—The salts of this acid were discovered by Margueritte,[1] but the acid was first prepared by Scheibler.[2] For this purpose the barium salt is decomposed by dilute sulphuric acid or the lead salt with sulphuretted hydrogen. Metatungstic acid crystallises in small yellow octahedra which lose their water of crystallisation at 100°, and on ignition are converted into the trioxide. They are readily soluble in water and the solution possesses a harsh, bitter taste. When the solution is concentrated by boiling, a white hydrate is deposited and afterwards the trioxide separates out. The metatungstates of the alkali metals are formed when the ordinary tungstates are boiled with tungstic acid until the filtrate gives no precipitate on addition of hydrochloric acid. The metatungstates of the other metals are, as a rule, easily soluble in water, and are best prepared by double decomposition of the barium salt with the corresponding sulphate or carbonate. The warm solutions usually yield the salts in amorphous masses when evaporated, but when concentrated over sulphuric acid they frequently crystallise. The metatungstates possess a bitter taste, and do not yield a precipitate on addition of an acid, though on continued boiling ordinary tungstic acid is deposited.

Colloidal Tungstic Acid.—This modification of tungstic acid was discovered by Graham,[3] and is obtained by dialysing a 5 per cent. solution of sodium tungstate to which sufficient hydrochloric acid has been added to combine with the sodium. The liquid remaining in the dialyser possesses a bitter astringent taste and does not gelatinise on the addition of acids, even on boiling. On evaporating in a vacuum a transparent gum-like mass is obtained, and this can be heated to 200° without losing its solubility, whilst at a red heat it is transformed into

[1] *Ann. Chim. Phys.*, 1846, [3], **17**, 475.
[2] *J. pr. Chem.*, 1861, **83**, 310. [3] *Journ. Chem. Soc.*, 1864, 325.

tungsten trioxide, losing 2·4 per cent. of water. When moistened with water the colloidal acid becomes pasty and adhesive like gum, dissolving completely in one quarter of its weight of water. It can also be obtained by dialysing a solution of freshly precipitated tungstic acid in oxalic acid.[1]

Sodium Tungstates.—The *normal salt,* $Na_2WO_4,2H_2O$, is prepared like the potassium salt, and is obtained on the large scale by fusing wolfram with soda ash. It crystallises in thin rhombic prisms which dissolve in four parts of cold and in two parts of boiling water.[2] The solution possesses a bitter taste and has an alkaline reaction. The crystals do not undergo alteration in the air, and they are insoluble in alcohol. When heated to 200° it becomes opaque and loses its water, and fuses at a red heat.

Sodium Paratungstate, $Na_{10}W_{12}O_{41},28H_2O$.—This salt, which is the one known commercially as tungstate of soda, is prepared on the large scale by roasting wolfram with soda ash and lixiviating the fused mass. The boiling solution is nearly neutralised with hydrochloric acid and allowed to crystallise at the ordinary temperature, when the salt separates in large triclinic crystals. At a higher temperature crystals containing 25 and 21 molecules of water are formed. This salt is sometimes used in place of sodium stannate as a mordant in dyeing and calico printing, and is also employed for rendering cotton, linen, "flannelette," &c., uninflammable.[3]

Sodium Metatungstate, $Na_2W_4O_{13},10H_2O$, is formed by prolonged boiling of the normal salt with tungsten trioxide. It crystallises in efflorescent octahedra probably belonging to the regular system. Cold water dissolves 10·69 times its weight of this salt, and boiling water dissolves it in all proportions. It loses its water at a red heat (Marignac and Scheibler).

Potassium Tungstates.—The *normal salt,* K_2WO_4, is obtained by adding tungsten trioxide little by little to its own weight of fused potassium carbonate. On cooling a solution of the fused mass in hot water, normal potassium tungstate crystallises in large acicular anhydrous crystals, or in large prismatic crystals, $K_2WO_4,2H_2O$ (Marignac). When the normal salt is boiled with a small quantity of water, or when tungsten trioxide is added

[1] Pappadà, *Gazz.*, 1902, **32**, ii., 22. Compare Sabanéeff, *Zeit. anorg. Chem.*, 1897, **14**, 354.

[2] Marignac, *Ann. Chim. Phys.*, 1863, [3], **69**, 39.

[3] Versmann, *Reports of the Juries of the Exhibition of* 1862.

to its boiling solution until no more dissolves, glistening scales of the *paratungstate*, $K_{10}W_{12}O_{41},11H_2O$, are deposited. These dissolve more readily in hot than in cold water, and the solution has an acrid taste and acid reaction. When alcohol is added to the aqueous solution a precipitate is formed; this dissolves on warming, but, on cooling, the solution deposits scales of *potassium metatungstate*, $K_2W_4O_{13},5H_2O$; a second hydrated salt containing $8H_2O$, crystallising in octahedra, is obtained from the mother-liquor of the normal tungstate.

Ammonium Tungstates.—The normal salt is extremely unstable.[1] When a solution of tungstic acid in ammonia is allowed to evaporate over caustic lime, warty concretions of $(NH_4)_8W_3O_{13},3H_2O$ are sometimes deposited, which easily give off ammonia. Needle-shaped crystals or tablets having the composition $(NH_4)_6W_7O_{24},6H_2O$ are, however, usually deposited, whilst sometimes small triclinic crystals of $(NH_4)_4W_5O_{17},5H_2O$ likewise occur. If, however, the ammoniacal solution of the trioxide be allowed to evaporate whilst warm, monoclinic crystals of $(NH_4)_{10}W_{12}O_{41},5H_2O$ separate out. When tungsten trioxide is boiled with ammonia, tetragonal prisms of *ammonium metatungstate*, $(NH_4)_2W_4O_{13},8H_2O$, are obtained. These are very soluble, and effloresce quickly on exposure to the air. Besides these many other ammonium tungstates have been prepared (Marignac), as well as compounds of these with ammonia, and ammoniacal derivatives of other tungstates.[2]

Normal Calcium Tungstate, $CaWO_4$.—This occurs native as scheelite in vitreous yellowish-white tetragonal pyramids. Some of its chief localities are Zinnwald, Caldbeck Fell in Cumberland, Piedmont, Dalecarlia, in the Vosges, at Huntingdon in Connecticut, and at the Mammoth mining district in Nevada. The crystals usually contain iron, and are found in crystalline rocks in connection with tin-ore, topaz, apatite, wolfram, &c.

It is prepared artificially as a white insoluble precipitate by mixing solutions of calcium chloride and a normal tungstate, and can be obtained in the crystalline form of scheelite by heating the precipitate mixed with lime in a current of hydrochloric acid. If a hot solution of metatungstic acid be saturated with calcium carbonate, calcium metatungstate, $CaW_4O_{13},10H_2O$, is obtained, crystallising in small tetragonal octahedra.

[1] Rosenheim and Jacobsohn, *Zeit. anorg. Chem.*, 1906, **50**, 297.

[2] Taylor, *J. Amer. Chem. Soc.*, 1902, **24**, 629; Briggs, *Journ. Chem. Soc.*, 1904, **85**, 672.

Lead Tungstate, $PbWO_4$, occurs as stolzite at Zinnwald in Bohemia, at Bleiberg in Carinthia, in Chili, and at Southampton, Massachusetts. It crystallises in red translucent tetragonal pyramids having a specific gravity of 7·87 to 8·13.

Ferrous Tungstate, $FeWO_4$, occurs as wolfram, $(Fe,Mn)WO_4$, which contains manganese as an isomorphous constituent, in Cornwall, Cumberland, Ireland, France, the Erzgebirge, and various parts of the United States. Wolfram crystallises in the monoclinic system in dark grey or brownish-black prisms having a metallic lustre and a specific gravity of 7·3.

Manganese Tungstate, $MnWO_4$, is found as hübnerite in Nevada in a vein from three to four feet wide.

Tungsten Tungstates.—By the partial reduction of tungsten trioxide a number of oxides of tungsten have been prepared, having a composition intermediate between that of the dioxide and trioxide. These have a blue or purple-red colour, and are probably combinations of the acidic trioxide with the more basic dioxide. Thus by the action of hydrogen on the trioxide at 250° the compound $W_3O_8 = 2WO_3,WO_2$ is formed, which has a deep blue colour; the same oxide, when prepared by heating ammonium metatungstate to a red heat, has a purple-red colour and metallic reflex.[1] Other blue oxides having the compositions $W_2O_5 = WO_2,WO_3$; $W_4O_{11} = 3WO_3,WO_2$; $W_5O_{14} = 4WO_3,WO_2$, have been described; in addition Desi has obtained oxides containing less oxygen than the dioxide, by the action of concentrated sulphuric acid on metallic tungsten under suitable conditions.

496 *Tungsten Bronzes.*—These remarkable compounds, obtained by the partial reduction of the tungstates, are usually regarded as compounds of the tungstates with tungsten dioxide, but their exact constitution is as yet unknown. Owing to their bronze-like appearance and insolubility in acids and alkalis, they have been employed as bronze powder substitutes.

They are scarcely affected by aqua regia, but are oxidised by ammoniacal silver nitrate solution, a reaction which is utilised for their analysis. Owing to their insolubility they can be freed from metallic tungsten and its oxides only by successive extractions with aqua regia, hydrochloric acid, potassium carbonate, and water.

[1] Desi, *J. Amer. Chem. Soc.*, 1897, **19**, 213; see also Hallopeau, *Compt. rend.*, 1898, **127**, 57; *Bull. Soc. chim.*, 1899, (3), **21**, 267; Allen and Gottschalk, *Amer. Chem. J.*, 1902, **27**, 328.

Tungsten Sodium Bronze was first obtained by Wöhler by the reduction of sodium tungstate with hydrogen, and may also be obtained by substituting coal-gas, zinc, iron, or tin for hydrogen, or by means of electrolysis. It forms fine golden cubes, which have a specific gravity of 6·617, and conduct electricity well. On ignition in the air it oxidises and fuses. It is not attacked by any acid except hydrofluoric acid, nor is it acted upon by alkalis.[1] According to Philipp,[2] the products are a mixture of different compounds, the relative proportions of which vary according to the method of preparation and the nature of the original tungstate. The substance obtained by heating the ditungstate in hydrogen, which was formerly supposed to have the composition $Na_2W_3O_9$, is according to Philipp, $Na_5W_6O_{18}$, and has a golden-yellow colour. By the electrolysis of fused sodium paratungstate a blue bronze, $Na_2W_5O_{15}$, is obtained, which forms dark blue cubes or plates having a red reflex. A purple-red bronze, $Na_2W_3O_9$, is obtained by strongly heating a mixture of 12·9 grams of sodium carbonate and 68·9 grams of tungsten trioxide with 20 grams of tinfoil, and a reddish-yellow bronze, $Na_4W_5O_{15}$, by fusing 60–80 grams of a mixture of two molecular proportions of sodium tungstate and one of the trioxide with 30 grams of tinfoil for two hours. It forms reddish-yellow cubes and yields a brownish-yellow powder.

Tungsten Potassium Bronze is obtained in a similar manner to the sodium bronzes, but only one compound[3] appears to exist, $K_2W_4O_{12}$. Bronzes containing lithium and rubidium have also been prepared as well as a number of mixed bronzes containing both sodium and potassium or an alkali metal along with one of the calcium group.[4]

497 *Phosphotungstic Acids.*—Tungstic acid combines with phosphoric, arsenic, antimonic, and vanadic acids to form complex substances analogous to the corresponding molybdic derivatives. A very large number of these have been prepared, the relation $R_2O_5 : WO_3$ varying from 1 : 7 to 1 : 24. *Phosphoduodecitungstic acid*, $H_3PW_{12}O_{40}.xH_2O$, is obtained by evaporating a mixture of the requisite quantities of orthophosphoric acid and metatung-

[1] Knorre, *J. pr. Chem.*, 1883, [2], **27**, 63.

[2] Philipp, *Ber.*, 1882, **15**, 499.

[3] Schaefer, *Zeit. anorg. Chem.*, 1904, **38**, 142, where references to the literature are given; Hallopeau, *Compt. rend.*, 1898, **127**, 57; *Bull. Soc. chim.*, 1899, [3], **21**, 267.

[4] See Engels, *Zeit. anorg. Chem.*, 1903, **37**, 125; Hallopeau, *Compt. rend.*, 1898, **127**, 512.

stic acid, or by the exact decomposition of the barium salt with sulphuric acid or of the mercurous salt with hydrochloric acid. It crystallises in tetragonal pyramids containing water of crystallisation, the amount of which is variously stated by different investigators. Phosphotungstic acid is largely used as a reagent for the precipitation of the alkaloids, proteins, and certain of their hydrolysis products, and also for the detection of potassium and ammonium salts, with which it yields insoluble precipitates. For this purpose it is prepared by acidifying a solution of 4 parts of sodium tungstate and 1 of common sodium phosphate with sulphuric acid and extracting the concentrated solution with ether, in which phosphotungstic acid is readily soluble.[1] Two sodium salts are known, having the formulæ $Na_2HPW_{12}O_{40},xH_2O$ and $Na_3PW_{12}O_{40},xH_2O$, and are obtained by heating together solutions of sodium hydrogen phosphate and tungstate. In presence of an excess of hydrochloric acid the former salt is obtained in yellow crystals, whilst when the acid is gradually added with stirring until crystallisation commences the latter salt separates out in transparent colourless octahedra.

The number of complex phosphotungstates and similar compounds is very large, and many of them crystallise well.[2]

498 *Silicotungstic Acids.*—These peculiar compounds were discovered and investigated by Marignac.[3]

Silicodecitungstic Acid, $H_8W_{10}SiO_{36},3H_2O(=4H_2O,SiO_2,10WO_3,3H_2O)$.—To prepare this acid, gelatinous silica is boiled with ammonium polytungstate and the solution evaporated, ammonia being added from time to time. The *ammonium salt*, $(NH_4)_8SiW_{10}O_{36},8H_2O$, is thus obtained in short rhombic prisms which are soluble in water; the solution is then precipitated by silver nitrate, the precipitate washed and decomposed by hydrochloric acid. On evaporating the filtrate in a vacuum the acid is left as a yellowish, glassy mass, and on exposure to

[1] Winterstein, *Chem. Zeit.*, 1898, **22**, 539.

[2] See Scheibler, *Ber.*, 1872, **5**, 801; Sprenger, *J. pr. Chem.*, 1880, [2], **22**, 48; Gibbs, *Amer. Chem. J.*, 1880, **2**, 217, 281; 1882, **4**, 377; 1883, **5**, 361, 391; 1885, **7**, 31, 392; Kehrmann, *Ber.*, 1887, **20**, 1805, 1811; 1891, **24**, 2326; 1892, **25**, 1966; *Annalen*, 1888, **245**, 45; *Zeit. anorg. Chem.*, 1891, **1**, 428; Drechsel, *Ber.*, 1887, **20**, 1452; Péchard, *Compt. rend.*, 1889, **109**, 301; 1890, **110**, 754; Hallopeau, *Compt. rend.*, 1896, **123**, 1065; Kehrmann and Rüttimann, *Zeit. anorg. Chem.*, 1899, **22**, 285; Rogers, *J. Amer. Chem. Soc.*, 1903, **25**, 298.

[3] *Ann. Chim. Phys.*, 1864, [4], **3**, 5.

air splits into fragments, which then deliquesce. Its salts have not been carefully examined.

On dissolving it in water and evaporating the solution, some silicic acid separates out, and the thick mother-liquor yields short triclinic prisms of *tungstosilicic acid*, $H_8W_{12}SiO_{42},20H_2O(=4H_2O,SiO_2,12WO_3,20H_2O)$, which are readily soluble in water and alcohol. It forms both normal and acid salts.

Normal Potassium Tungstosilicate, $K_8W_{12}SiO_{42},20H_2O$, crystallises in ill-defined rhombic prisms.

Acid Potassium Tungstosilicate, $H_4K_4W_{12}SiO_{42},7H_2O$, occurs in two different forms, which crystallise from the same solution, and if one form be dissolved in water, the second form frequently crystallises out. The α-compound forms transparent, thick, rhombic prisms, and the β-compound crystallises in silky, soft, six-sided rhombic plates.

Silicoduodecitungstic or *Silicotungstic Acid* was formulated by Marignac as an octabasic acid $H_8SiW_{12}O_{42},29H_2O(=4H_2O,SiO_2\ 12WO_3,29H_2O)$, but according to Wyrouboff[1] it is tetrabasic, and has the formula $2H_2O,SiO_2,12WO_3,31H_2O$, the normal salts of Marignac being basic salts and his acid salts in reality the normal salts. All the salts contain water of crystallisation, and in view of the uncertainty as to their constitution are at present best formulated in terms of the oxides. The salts of this acid are formed by boiling gelatinous silicic acid with the polytungstates of the alkali metals. To obtain the acid the salts are precipitated with mercurous nitrate and the washed precipitate decomposed by hydrochloric acid. It crystallises below 40° in large tetragonal pyramids of the formula $H_8SiW_{12}O_{42},29H_2O$, above 40°, or in presence of hydrochloric acid, in rhombohedral forms, $H_8SiW_{12}O_{42},22H_2O$, and readily dissolves in water, alcohol, and ether. Silicotungstic acid is a valuable reagent for alkaloids.

The salts, with the exception of the mercurous salt and a few others, are soluble in water. Boiling hydrochloric acid converts the normal salts into acid salts without decomposing them further (Marignac), whilst alkalis decompose their solutions with the separation of silicic acid. They have been very thoroughly examined both by Marignac and Wyrouboff.

Potassium Silicotungstate.—Three distinct salts are known. The salt $4K_2O,SiO_2,12WO_3,14H_2O$ forms hard granular crusts,

[1] *Bull. Soc. franc. Min.*, 1896, **19**, 219.

consisting of prisms closely resembling cubes; $2K_2O,SiO_2,12WO_3,18H_2O$ forms transparent glistening, hexagonal crystals; and $3K_2O,2SiO_2,24WO_3,30H_2O$ crystallises in monoclinic prisms.

Marignac formulates the first of these as the normal salt, $K_8SiW_{12}O_{42},14H_2O$, and the others as acid salts, $H_4K_4SiW_{12}O_{42}16H_2O$ and $2H_5K_3SiW_{12}O_{42},25H_2O$, whereas Wyrouboff regards them as a basic salt, $K_4SiW_{12}O_{40},4KHO,12H_2O$, a normal salt, $K_4SiW_{12}O_{40},18H_2O$, and a double salt, $K_4SiW_{12}O_{40},K_2H_2SiW_{12}O_{40},29H_2O$.

Zircono-,[1] mangano-,[2] and silico-vanadio-tungstates[3] have also been obtained.

Pertungstic Acid.—When a solution of sodium paratungstate is boiled for a few minutes with hydrogen peroxide, a yellowish solution is obtained, which no longer gives a precipitate with nitric acid.[4] When the solution is allowed to evaporate in a vacuum, small white crystals having the formula $NaWO_4,H_2O$ are deposited, which are the sodium salt of the unknown pertungstic acid, HWO_4. The same salt is formed in solution by the electrolysis of slightly acid solutions of sodium tungstate.[5] More highly oxidised compounds are formed by the action of caustic alkali and hydrogen peroxide on a solution of a pertungstate,[6] the unstable salts Na_2O_2,WO_4,H_2O_2; $Na_2O_2,WO_4,H_2O_2,(Na_2O_2)_2WO_4,7H_2O$; and K_2O_4,WO_4,H_2O having been isolated in this way. Aqueous solutions of pertungstic acid and hydrogen peroxide appear to contain the unstable acids[7] $WO_2(O_2H)_2$ and $WO_2(O_2H)(OH)$.

Tungsten and the Halogens.

499 *Tungsten Hexafluoride*, WF_6, is formed by the action of anhydrous hydrofluoric acid on tungsten hexachloride in the cold, and can also be prepared by the action of arsenic trifluoride or antimony pentafluoride on the hexachloride. The preparation by the last of these methods can be carried out in glass vessels and proceeds according to the equation:

$$WCl_6 + 3SbF_5 = WF_6 + 3SbF_3Cl_2.$$

[1] Hallopeau, *Bull. Soc. chim.*, 1896, [3], **15**, 917.
[2] Just, *Ber.*, 1903, **36**, 3619.
[3] Friedheim and Henderson, *Ber.*, 1902, **35**, 3242.
[4] Péchard, *Compt. rend.*, 1891, **112**, 1060.
[5] Thomas, *J. Amer. Chem. Soc.*, 1899, **21**, 373.
[6] Melikoff and Pissarjewsky, *Ber.*, 1898, **31**, 632.
[7] Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 472.

Antimony pentafluoride is gradually added to the tungsten hexachloride contained in a flask until no further reaction occurs, and the contents of the flask are finally heated to 90°. The hexafluoride volatilises, and is condensed in a receiver cooled by a freezing mixture of alcohol and solid carbon dioxide. A trace of chlorine is present, which can be removed by allowing the liquid in the receiver to boil for a moment.[1]

Pure tungsten hexafluoride is a colourless gas, which has the normal density corresponding with the formula WF_6, and is therefore about ten times as heavy as air. It condenses to a faintly yellow liquid which boils at 19·5° and solidifies at 2·5° to a snow-white mass. It is at once decomposed by water and fumes in the air; nearly all the commoner metals, except gold and platinum, are attacked by it. It is absorbed by alkali fluorides and reacts violently with ammonia.

Tungsten Oxytetrafluoride, WOF_4, can be prepared by the action of anhydrous hydrofluoric acid on the oxytetrachloride in the cold, or by heating tungsten trioxide with lead fluoride to redness in an electric furnace. It sublimes in white plates, melts at 110°, and boils at 185–190°. It is decomposed by water, and is soluble in chloroform, absolute alcohol, and benzene. It appears to unite with ammonia, forming an orange-coloured substance (Ruff).

Tungsten Dioxydifluoride, WO_2F_2, has not been prepared pure, but is formed in small amount by the action of moisture on the vapour of the oxytetrafluoride. Double salts with the alkali fluorides, such as $2KF,WO_2F_2,H_2O$, have, however, been prepared by the action of hydrofluoric acid on the tungstates.[2] A double salt of the formula KF,WO_2F_2,H_2O is also known.

500 Four compounds of tungsten and chlorine are known, viz.:

(1) Tungsten dichloride . . . WCl_2.
(2) Tungsten tetrachloride . . WCl_4.
(3) Tungsten pentachloride . . WCl_5.
(4) Tungsten hexachloride . . WCl_6.

Tungsten Dichloride, WCl_2.—This body may be obtained in pale grey crusts by reducing the hexachloride in hydrogen at a moderately high temperature. It is, however, best prepared by

[1] Ruff and Eisner, *Ber.*, 1905, **38**, 742; Ruff, Eisner, and Hiller, *Zeit. anorg. Chem.*, 1907, **52**, 256.

[2] Marignac, *Ann. Chim. Phys.*, 1863, [3], **69**, 70.

heating the tetrachloride in a current of carbon dioxide at the temperature of a moderately hot zinc bath. The dichloride is a non-volatile loose grey powder without lustre or crystalline structure. It alters perceptibly on short exposure to the air and dissolves slightly in water forming a brown solution. The remainder is converted into the brown oxide, a slow evolution of hydrogen occurring (Roscoe).

Tungsten Tetrachloride, WCl_4, is produced by the incomplete reduction of the hexachloride or pentachloride by hydrogen, and forms the non-volatile residue obtained by the distillation of the hexachloride in hydrogen. In order to obtain it in the pure state a mixture of hexa- and penta-chloride is distilled at a low temperature from a bath of sulphuric acid in a current of dry hydrogen or carbon dioxide, and the volatile pentachloride poured back again once or twice over the residue to convert into the tetrachloride the lower chlorides or metal which are also formed. Tungsten tetrachloride is a loose, soft, crystalline powder of a greyish-brown colour. It is highly hygroscopic, though not so much so as the pentachloride, and is partially decomposed by cold water into the brown oxide and hydrochloric acid. The tetrachloride is non-volatile and infusible under ordinary pressure, but on heating it decomposes into pentachloride, which distils off, and dichloride, which remains behind. On heating in hydrogen to a temperature above the melting point of zinc the tetrachloride is reduced to metallic tungsten, some of which is deposited as a black tinder-like powder and undergoes spontaneous ignition on exposure to air (Roscoe).

Tungsten Pentachloride, WCl_5.—This compound is formed by the incomplete reduction of the hexachloride in a current of hydrogen. If the temperature be kept but slightly above the boiling point of the hexachloride the dark-red colour of its vapour is seen to disappear and a light greenish-coloured vapour takes its place, and this soon condenses either to black drops or to long shining black needle-shaped crystals. After two or three distillations in hydrogen a pure volatile product is obtained. For the production of the pentachloride, it is, however, more convenient to reduce the hexachloride at a higher temperature, when a further loss of chlorine takes place, the solid non-volatile tetrachloride remaining behind and the volatile pentachloride distilling over. The latter compound only requires redistillation in order to be obtained in the pure state. Tungsten pentachloride crystallises in long black shining crystals, but if

quickly condensed the crystalline powder possesses a dark-green colour, resembling potassium manganate. It melts at 248°, boils at 275·6°, has the normal vapour density at 350°, and is extremely hygroscopic, the crystals becoming instantly covered with a dark golden-green film on exposure to air, whilst the small particles are converted into liquid. The crystals do not decrepitate on cooling like those of the hexachloride. On treatment with large quantities of water, the pentachloride forms an olive-green solution, although the greater part is at once decomposed into the blue oxide and hydrochloric acid.

Tungsten Hexachloride, WCl_6.—This substance is prepared by heating metallic tungsten in an excess of dry and pure chlorine. It is necessary for the preparation of the pure compound that every trace of oxygen and of moisture be excluded, as otherwise some red oxychloride is invariably formed, and this cannot easily be separated from the hexachloride by distillation. Metallic tungsten takes fire at a moderate heat in dry chlorine, and the action goes on by itself until all the chlorine has disappeared.

In order to obtain the hexachloride in quantity the metal is first ignited in a current of dry hydrogen; then the hydrogen is completely displaced by a current of dry carbon dioxide and lastly chlorine free from air substituted, and the tube or retort moderately heated. At the commencement of the operation a slight sublimate of red needle-shaped crystals of the oxychloride is frequently formed owing to the unavoidable presence of traces of oxygen, but this is easily driven to the end of the tube beyond the point at which it is intended to collect the hexachloride. On raising the temperature of the metal, a granular sublimate of dark-violet opaque crystals of the hexachloride makes its appearance, and if in large quantity the hexachloride collects as a blackish-red liquid. In order to saturate this liquid, it is slowly distilled in a current of chlorine. The dark-violet crystals decrepitate on cooling, and the crystalline mass thus readily breaks up into a powder.

When pure, the solid hexachloride does not undergo any change even in moist air, but in the presence of the slightest trace of oxychloride it at once absorbs moisture, evolving copious fumes of hydrogen chloride and changing in colour from violet to brown. Water does not act upon the pure hexachloride, but on boiling decomposition occurs. If, however, the oxychloride be present the whole is suddenly decomposed by cold water into a greenish

oxide. It is soluble in carbon disulphide and crystallises from the solution in six-sided plates.

The melting point of the hexachloride is 275°; it boils under a pressure of 759·5 mm. at 346·7°. The vapour density of tungsten hexachloride has been determined in sulphur vapour and in mercury vapour; at 440°, the mean experimental density compared with that of hydrogen is 168·8, whilst at 350° the density is 190·9, the calculated density being 196·9. The alteration of the density from 191 at 350°, only 3° above the boiling point, to 169 at 440° points to the fact that dissociation occurs. That this is the case is shown by the fact that when a current of dry carbon dioxide is passed through the fused hexachloride a continuous liberation of chlorine takes place, whereas the pentachloride treated in the same way does not undergo a similar decomposition.

Tungsten Oxychlorides.—The *oxytetrachloride* $WOCl_4$, and the *dioxydichloride* WO_2Cl_2, have been studied by Blomstrand and Riche. The dioxydichloride is best obtained by passing chlorine over the brown oxide, WO_2. Combination takes place at a moderate temperature, the oxide becoming covered with a whitish crust, which as the temperature increases sublimes without melting, condensing in small square scales of a light lemon-yellow colour. The dioxydichloride volatilises at a temperature approaching redness with partial decomposition; the crystals do not fuse, and are not acted upon by moist air or cold water. Even when boiled with water the dioxydichloride is not completely decomposed.

The splendid red needle-shaped crystals of the oxytetrachloride, first prepared by Wöhler, are obtained by passing the vapour of the hexachloride over heated oxide or dioxydichloride:

$$WO_3 + 2WCl_6 = 3WOCl_4,$$

and also by acting on the trioxide with phosphorus pentachloride.[1] The crystals melt at 210°·4, and the liquid boils at 227°·5, forming a red vapour rather lighter coloured than that of the hexachloride, and having the normal density at 350° (Roscoe). On repeated distillation over red-hot charcoal in a current of chlorine the hexachloride is formed. On exposure to the air the oxytetrachloride becomes at once covered with a yellowish crust of tungstic acid.

[1] Schiff, *Annalen*, 1879, **197**, 185.

501 Bromine acts rapidly on red-hot tungsten, forming dark bromine-like vapours, which condense to a crystalline sublimate. Special precautions similar to those taken in the preparation of the chlorides must also be employed for the bromides, as the oxybromides formed in the presence of air and moisture possess almost the same colour as the bromide, and therefore the detection of the impurity is not so easy as is the case with the chloride.

Tungsten Dibromide, WBr_2, is formed by the reduction in hydrogen of the pentabromide, heated in a bath of fused zinc chloride. A residue of non-volatile dibromide remains in the form of a bluish-black velvety crystalline powder.

Tungsten Pentabromide, WBr_5, is prepared by the action of an excess of bromine on tungsten, and is formed also when the hexachloride is heated in dry hydrogen bromide, but cannot be prepared pure in this way.[1] The pentabromide forms dark crystals having a metallic lustre resembling iodine, melting at 276°, and boiling at 333°. It is at once decomposed by an excess of water into hydrobromic acid and the blue oxide. When the pentabromide is heated in a current of hydrogen, the metal is formed in the state of pyrophoric powder. Liquefied hydrogen bromide converts the hexachloride at 60–70° into a mass of olive-green crystals which melt at 232° and have the composition $WCl_6,3WBr_6$, whilst at the ordinary temperature a similar substance of the composition WCl_6,WBr_6 is formed (Defacqz).

Tungsten Hexabromide, WBr_6, is obtained, according to Schaffer and Smith,[2] by gently heating tungsten in dry bromine vapour in an atmosphere of nitrogen. It can be sublimed, and forms blue-black needles. It decomposes very readily when heated, fumes in the air, and is decomposed by water with formation of a blue oxide.

Tungsten Oxybromides, corresponding to the oxychlorides, exist. The *dioxydibromide,* WO_2Br_2, is prepared by passing bromine vapour over red-hot tungsten dioxide. It forms light-red transparent crystals which yield a yellow powder. They do not melt, but volatilise at a temperature approaching a red heat, and are not acted upon by water. The *oxytetrabromide,* $WOBr_4$, is formed under the same circumstances as the last-named compound in brownish-black shining needles, which are readily

[1] Defacqz, *Ann. Chim. Phys.*, 1901, [7], **22**, 247.
[2] *J. Amer. Chem. Soc.*, 1897, **18**, 1098.

fusible and can be separated from the dioxydibromide by gently heating, when the latter compound remains behind. It melts at 277°, boils at 327°·5, and is decomposed by contact with water.

Tungsten Di-iodide, WI_2, is obtained in the form of green metallic scales, when iodine vapour is passed over the metal heated to redness (Roscoe), and is formed also by the action of hydrogen iodide on the hexachloride at 400° (Defacqz).

Tungsten Tetra-iodide, WI_4, has been obtained by Defacqz by the action of liquefied hydrogen iodide on the hexachloride at 100°, and is a black infusible crystalline mass, which is decomposed by water into the brown oxide and hydriodic acid.

Tungsten and Sulphur.

502 *Tungsten Disulphide*, WS_2, is obtained by the action of sulphur, sulphuretted hydrogen, or carbon disulphide on ignited metallic tungsten. It may be prepared also by heating tungsten trioxide in a crucible with six times its weight of cinnabar or with potassium carbonate and sulphur, and by heating the hexachloride in a current of sulphuretted hydrogen (Defacqz). It forms soft, black, needle-shaped crystals which soil the fingers like graphite.

A *chlorosulphide*, $WCl_6,3WS_3$, is formed by the action of liquefied sulphuretted hydrogen on the hexachloride at 60° (Defacqz).

Tungsten Trisulphide, WS_3, is obtained only in the wet way by dissolving tungsten trioxide in ammonium sulphide and precipitating with an acid, or by saturating an aqueous solution of an alkali tungstate with sulphuretted hydrogen, and acidifying. When dry it is black, yielding a liver-coloured powder. It dissolves slowly in cold water, and is precipitated by ammonium chloride and acids. It is easily dissolved by potassium carbonate and also by ammonia. When heated with cyanide of potassium it is converted into the disulphide, which latter compound is unaltered by fusion with excess of this reagent.

The Thiotungstates.—The thiotungstates of the alkali and alkaline earth metals are prepared by dissolving the trisulphide in the corresponding hydrosulphide, or by treating the corresponding tungstate with sulphuretted hydrogen. The ammonium salt, $(NH_4)_2WS_4$, is deposited from concentrated

solution in yellowish-red crystals; the potassium salt, K_2WS_4, forms anhydrous yellow crystals, whilst the sodium salt, Na_2WS_4, crystallises with difficulty.

Tungsten and Nitrogen, Phosphorus, Carbon, Silicon, and Boron.

503 Tungsten does not combine directly with nitrogen, and neither the metal nor the dioxide is attacked when strongly heated in ammonia. By the action of ammonia on the oxytetrachloride or the hexachloride in the cold, a black semi-metallic powder is obtained, which has the composition W_2N_3. It is insoluble in caustic soda, nitric acid, and dilute sulphuric acid, but is converted by concentrated sulphuric acid into ammonia and tungstic acid.[1]

By the action of ammonia on tungsten trioxide at a dull red heat Wöhler obtained a black amorphous product which he termed *tungsten nitretamidoxide*, the formula of which is $W_5N_6H_3O_5$ (Rideal). It is insoluble in acids and alkalis, but dissolves in sodium hypochlorite, and on ignition decomposes, ammonia, nitrogen, and hydrogen being evolved.

Phosphides of Tungsten.—Phosphorus and tungsten combine directly when the finely powdered metal is heated to redness in phosphorus vapour, a dark green powder of the composition W_3P_4 being formed. Another compound, W_2P, is obtained, when a mixture of phosphorus pentoxide and tungsten trioxide, in the proportion of two molecules of the former to one molecule of the latter, is reduced at a high temperature in a charcoal crucible,[2] and forms a vesicular mass, the hollow portions of which contain large crystals.

A black amorphous *diphosphide*, WP_2, is formed when the hexachloride is heated in phosphine, and this reacts with copper phosphide at a high temperature to form *tungsten monophosphide* WP, which crystallises in grey prisms with a metallic reflex, has the sp. gr. 8·5, and is oxidised to tungsten trioxide when heated in air (Defacqz). An *arsenide*, WAs_2, has also been prepared in a similar manner to the diphosphide, which it resembles in properties.

Tungsten and Carbon.—Tungsten forms two carbides.

[1] Wöhler, *Annalen*, 1850, **73**, 190; 1858, **105**, 258; Rideal, *Journ. Chem. Soc.*, 1889, **55**, 41.

[2] Wöhler, *Journ. Chem. Soc.*, 1853, **94**.

The compound obtained by heating the oxide with carbon or calcium carbide [1] has the formula W_2C, whilst in presence of a large amount of iron [2] the carbide WC is produced. They are both hard, iron-grey, crystalline substances. Several complex carbides containing iron or chromium have also been prepared.[3]

Tungsten Silicide, W_2Si_3, is obtained by heating the trioxide with silicon in the electric furnace,[4] and freeing the product from metal by electrolytic oxidation. It forms beautiful steel-grey plates with a metallic lustre, has the sp. gr. 10·9, and burns in oxygen. It is attacked by a mixture of nitric and hydrofluoric acids, and by fused potash.

Tungsten Boride, WB_2, is obtained by fusing the two elements together, and crystallises in hard octahedra of sp. gr. 9·6. It is attacked by concentrated acids.[5]

Detection and Estimation of Tungsten.

504 All the insoluble tungsten compounds can be converted into soluble tungstates by fusion, either with a caustic alkali alone, or with the addition of nitre. The solution when brought into contact with zinc and hydrochloric acid becomes blue-coloured, owing to the formation of the blue tungsten oxides (or tungsten tungstates), and when ammonium sulphide is added to the colourless solution, and then dilute hydrochloric acid, a brown precipitate of tungsten sulphide is obtained, whereas hydrochloric acid alone precipitates tungstic acid, which on heating turns yellow. If the tungsten compounds are fused with a small quantity of tin in the reducing flame with microcosmic salt, a blue bead is obtained, whilst tungsten compounds containing iron yield in the reducing flame a blood-red bead. Tungstic oxide can be very readily detected by fusing with potassium bisulphate and adding sulphuric acid and a crystal of phenol or quinol (hydroquinone), when a blue or violet coloration is produced, by the aid of which the presence of 0·002 mgm. of tungstic oxide can be recognised (Defacqz).

Tungsten is estimated *gravimetrically* as the trioxide. For

[1] Moissan, *Compt. rend.*, 1896, **123**, 13 ; 1897, **125**, 839.

[2] Williams, *Compt. rend.*, 1898, **126**, 1722.

[3] *Compt. rend.*, 1898, **127**, 1410 ; 1899, **128**, 207 ; 1903, **137**, 292.

[4] Vigoroux, *Compt. rend.*, 1898, **127**, 393. See also Warren, *Chem. News*, 1898, **78**, 318.

[5] Tucker and Moody, *Journ. Chem. Soc.*, 1902, **81**, 16.

the purpose of ascertaining the quantity contained in wolfram, for instance, the finely powdered mineral is heated with aqua regia, evaporated to dryness, the residue treated with water, the soluble chlorides of iron and manganese filtered off, and the insoluble tungstic acid washed with alcohol and dissolved in ammonia. The solution is then evaporated down, and the residue heated gently, and afterwards ignited in presence of air, when the trioxide remains, and is weighed. Solutions of tungstates may also be precipitated with benzidine hydrochloride [1] or mercurous nitrate,[2] and the precipitate ignited and weighed as the trioxide (compare also Wolter).[3]

Atomic Weight of Tungsten.—The atomic weight of tungsten has been determined by numerous investigators. Schneider,[4] by the reduction of tungsten trioxide to metal and oxidation of the metal to trioxide, found the average value 184·11, whilst Marchand [5] found an almost identical value. Roscoe [6] by the same method obtained the number 183·48, and by the analysis of the hexachloride the number 184·02, whilst Waddell [7] by the reduction of the trioxide found the higher number 184·33. More recently Pennington and Smith and Desi [8] have found the still higher number 184·8 by Schneider's method, but their results have been criticised by Schneider [9] as untrustworthy. The investigations carried out by Smith and Exner,[10] who converted the hexachloride into the trioxide by the action of water and synthesised the trioxide from the metal, gave an average value for the atomic weight of 184·06. The value now (1913) adopted is 184·0.

URANIUM. U = 238·5.

505 The mineral known as pitchblende was formerly believed by certain chemists to be an ore of either zinc or iron, whilst by others it was thought to contain tungsten. Klaproth, in 1789, was the first to point out the existence in this mineral of a peculiar metal, to which he gave the name of uranium, in re-

[1] v. Knorre, *Ber.*, 1905 **38**, 783.
[2] Defacqz, *Compt. rend.*, 1896, **123**, 308.
[3] *Chem. Zeit.*, 1910, **34**, 2.
[4] *J. pr. Chem.*, 1850, **50**, 152.
[5] *Annalen*, 1851, **77**, 261.
[6] *Mem. Manch. Phil. Soc.*, [3], **5**, 77; *Annalen*, 1872, **162**, 366.
[7] *Amer. Chem. J.*, 1886, **8**, 280.
[8] *Zeit. anorg. Chem.*, 1895, **8**, 198, 205.
[9] *J. pr. Chem.*, 1896, [2], **53**, 288.
[10] *J. Amer. Chem. Soc.*, 1904, **26**, 1082.

membrance of Herschel's discovery of the planet Uranus, in the year 1781. The body obtained by Klaproth by the reduction of the calx of uranium was supposed by all the chemists who subsequently investigated the subject to be the metal, until Péligot [1] in 1842 proved this body to be an oxide. Péligot likewise isolated the metal and determined its equivalent.

Uranium is not a very abundant element, and its chief ore is pitchblende or uraninite. This consists of impure uranoso-uranic oxide, U_3O_8, and is found in Cornwall, at Joachimsthal, Johanngeorgenstadt, Adrianople, and other localities. Uranium is found also as phosphate in uranite or uranium-mica, as carbonate in liebigite, voglite, and uranothallite, whilst as uranotantalite or samarskite (p. 776) it is found combined with columbium and tantalum, and in carnotite with vanadium. Pitchblende is the best source of uranium, this mineral usually containing from 40 to 90 per cent. of uranoso-uranic oxide, U_3O_8. The following analysis by Ebelmen gives the composition of an average specimen of pitchblende:

Uranoso-uranic oxide, U_3O_8	75·23
Lead sulphide	4·82
Silica	3·48
Lime	5·24
Magnesia	2·07
Soda	2·05
Ferrous oxide	3·10
Manganous oxide	0·82
Carbon dioxide	3·32
Water	1·85
	101·98.

The uranium minerals always contain the radioactive element radium, as well as helium, the occurrence of which is discussed under the heading of Radioactive Elements. Small amounts of compounds of copper, bismuth, silver, zinc, arsenic, and aluminium are often present.

The process recommended by Wöhler for the extraction of uranium from pitchblende is as follows: The powdered mineral is digested with sulphuric acid, small quantities of nitric acid being added from time to time to the mixture. As soon as the precipitate is transformed into a white powder and partially dis-

[1] *Ann. Chim. Phys.*, 1842, [3], **5**, 5.

solved, the excess of sulphuric acid is driven off, and the residue digested with water. This leaves a residue of silica, lead sulphate, and the basic sulphates and arsenates of bismuth. The filtered liquid is warmed, and a current of hydrogen sulphide passed through it, when arsenic, antimony, copper, and the rest of the lead and bismuth are thrown down. The filtrate is then oxidised by nitric acid, and an excess of ammonia added; the precipitate containing the ferric and uranic hydroxides is next washed with ammonia, and digested at 100° with a concentrated solution of ammonium carbonate containing an excess of ammonia. The uranic hydroxide dissolves, and the yellow double carbonate of uranium and ammonium crystallises out on cooling. The mother-liquor still contains a small quantity of uranium, together with cobalt, nickel, and zinc, and these latter metals are precipitated by ammonium sulphide, which is added drop by drop until no further brown precipitate falls. The filtered liquid is boiled, and this soon deposits a yellow precipitate of ammonium uranate. Another process described by Péligot depends upon the facility with which uranyl nitrate crystallises, and upon its ready solubility in ether. Finely powdered pitchblende is treated with nitric acid, the acid solution evaporated to dryness, and the residue washed with water, leaving a residue consisting chiefly of lead sulphate and ferric oxide and arsenate. The filtered liquid has a greenish-yellow colour, and yields on concentration a radiated crystalline mass. This is then dried, the mother-liquor evaporated, and the whole again crystallised. Long prismatic crystals are thus deposited, which must be washed with a small quantity of cold water, the washings being again used for dissolving another portion of the crude nitrate. After having been dried, the crystals are shaken up with ether, when uranyl nitrate dissolves; it is obtained in the form of crystalline needles on evaporation of the ethereal solution.

Metallic Uranium was first prepared in the pure state by Péligot, who obtained it by the action of sodium or potassium on uranium tetrachloride, a mixture of the tetrachloride, potassium chloride, and sodium being usually employed.[1] It is however, best obtained by heating 500 parts of the oxide, U_3O_8, with 40 parts of sugar charcoal in the electric furnace in a carbon tube, closed at one end. The product contains a little carbon, which is partially removed by heating it in a crucible

[1] *Ann. Chim. Phys.*, 1869, [4], **17**, 368.

brasqued with uranium oxide, and enclosed in a larger crucible brasqued with titanium to protect the uranium from the action of nitrogen.[1] Uranium may also be obtained by heating the dioxide to redness with carbon and starting the reduction by means of a cartridge of magnesium and barium dioxide,[2] or by reducing the trioxide with aluminium in the presence of liquid air, a fused regulus of the metal containing a little aluminium being thus obtained.[3]

Pure uranium has a white colour, and takes a high polish; it has a specific gravity of 18·7 at 14°, and a specific heat of 0·02765; in the powdered state it oxidises on exposure to the air and decomposes water slowly at the ordinary temperature, and more quickly at the boiling point. In the same condition it burns in oxygen at 170°, in fluorine at the ordinary temperature, in chlorine at 180°, in bromine at 210°, in iodine at about 260°, and in sulphur vapour at 500°. It melts at a high temperature, and has a higher boiling point than iron, condensing in small, non-magnetic spheres, free from carbon.[4] It readily combines with nitrogen at 1000°.

Several alloys with iron, manganese, and cobalt have been prepared by the aluminium reduction method. An amalgam[5] can be obtained by the electrolytic method, and leaves a residue of pyrophoric uranium when the mercury is distilled off at 242°.

Metallic uranium and its compounds are radioactive.

COMPOUNDS OF URANIUM.

Uranium and Oxygen.

506 Uranium combines with oxygen to form two well-defined oxides, UO_2 and UO_3, and these combine, forming intermediate oxides. The dioxide is a basic oxide, and gives rise to the uranous salts, in which the metal is tetravalent. The trioxide, like the corresponding oxide of the other metals of this group,

[1] Moissan, *Compt. rend.*, 1896, **122**, 1088.

[2] Aloy, *Bull. Soc. chim.*, 1901, [3], **25**, 344.

[3] Stavenhagen, *Ber.*, 1899, **32**, 3065; Stavenhagen and Schuchard, *ibid.*, 1902, **25**, 909.

[4] Zimmermann, *Annalen*, 1883, **216**, 1; Moissan, *Compt. rend.*, 1893, **116**, 1429; 1896, **122**, 1088; 1906, **142**, 425.

[5] Férée, *Bull. Soc. chim.*, 1901, [3], **25**, 622.

behaves as an acid-forming oxide, yielding salts known as the *uranates*, analogous to the chromates, molybdates, and tungstates. Like the other trioxides of the group, uranium trioxide also yields a large number of derivatives in which only one of the three oxygen atoms is replaced by negative groups; these may be regarded as derivatives of the divalent compound radical *uranyl*, UO_2. This radical has more decidedly basic properties than the corresponding radicals derived from the other metals, and the derivatives, therefore, correspond to the salts of a basic oxide, whilst the similar compounds of the other metals are more nearly allied to the acid chlorides, such as sulphuryl chloride, SO_2Cl_2, and phosphoryl chloride, $POCl_3$. This view of the constitution of the uranyl salts is supported by the electrochemical properties of their solutions. In aqueous solution the salts of strong acids, $UO_2.R'_2$, are hydrolysed to a small extent, corresponding in this respect to the analogous salts of aluminium and glucinum. The non-hydrolysed portion of the salt dissociates in the normal manner, and on electrolysis the uranyl ion migrates to the cathode. Complex derivatives are, however, very readily formed, especially with salts of organic acids.[1] As already mentioned, it was long supposed that the dioxide was the free metal, and what is now known as the trioxide was regarded as a compound of the metal with one atom of oxygen.

Uranium dioxide, UO_2.—This oxide, formerly mistaken for the metal uranium, is obtained by heating uranoso-uranic oxide, U_3O_8, or uranic oxalate in a current of hydrogen, or by the electrolysis of uranyl nitrate solution under suitable conditions.[2] Thus prepared it is a pyrophoric powder, having a brown or copper-red colour, and a specific gravity of 10·15. When heated in the air it takes fire, and is completely converted into the oxide, U_3O_8. It dissolves in strong acids, forming the green uranous salts. It may be obtained in jet black octahedra isomorphous with thoria by fusing with borax, and then removing the latter with dilute hydrochloric acid.[3] It is also formed in microscopic, black, non-pyrophoric crystals when crystalline uranic hydroxide is reduced in hydrogen,[4] and is

[1] Dittrich, *Zeit. physikal. Chem.*, 1899, **29**, 449; Ley, *ibid.*, 1900, **30**, 193; *Ber.*, 1900, **33**, 2658. Compare Kohlschütter, *Annalen*, 1900, **311**, 1.

[2] Oechsner de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, 321.

[3] Hillebrand, *Zeit. anorg. Chem.*, 1893, **3**, 249.

[4] Aloy, *Bull. Soc. chim.*, 1900, [3], **23**, 368.

left as a brick-red mass, which becomes black on heating, when uranyl bromide is heated in the air.[1]

Uranous Hydroxide, $UO_2,2H_2O$, is precipitated in reddish-brown flakes, which become black on ebullition, by adding an alkali to a uranous solution.[2] It dissolves easily in dilute acids, whilst the calcined oxide is only slightly soluble in these liquids.

Uranic Oxide, UO_3, or *Uranyl Oxide,* $(UO_2)O$.—When uranyl nitrate is heated in a glass tube to 250° so long as acid fumes escape, this oxide is left behind in the form of a brownish-yellow powder, whereas, when the nitrate is rapidly decomposed, a red modification of the oxide is produced.[3]

Uranic Hydroxide, $UO_3,2H_2O$, cannot be obtained by precipitating a uranyl salt by an alkali, the precipitate thus formed consisting of an alkali uranate. It may, however, be prepared, according to Berzelius, by gently calcining the nitrate in a sand-bath as long as nitric acid is evolved. The residue contains uranic hydroxide mixed with a basic salt, which can be removed by washing with boiling water. It may likewise be obtained by evaporating a solution of uranyl nitrate in absolute alcohol, at a moderate heat, until a yellow mass remains, consisting of the hydroxide, $UO_2(OH)_2,H_2O$. This hydrate loses half its water at 100°, or in a vacuum at the ordinary temperature, but at a temperature of 400° it begins to lose oxygen, and is converted into uranoso-uranic oxide, U_3O_8. Uranic hydroxide is yellow, and has a specific gravity of 5·92. It does not undergo change in the air, nor does it absorb carbon dioxide.

An orange-coloured hydroxide, UO_3,H_2O, can be obtained by the electrolysis of the nitrate,[4] and is formed in rhombic crystals when the violet hydrate of the oxide U_3O_8 is boiled with water in the air.[5]

This oxide, as mentioned above, yields by the action of acids the *uranyl* salts, whilst with bases it gives rise to the *uranates.* The former have a yellow colour, and most of them possess a remarkable fluorescence, which they impart to glass. The absorption bands exhibited by these compounds have been studied by Becquerel and others. These salts are highly sensi-

[1] Oechsner de Coninck, *Compt. rend.*, 1902, **135**, 900.

[2] See Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 613.

[3] Oechsner de Coninck, *Compt. rend.*, 1901, **132**, 204; *Bull. Acad. roy. Belg.*, 1904, 363, 448.

[4] Oechsner de Coninck and Camo, *Bull. Acad. roy. Belg.*, 1901, **3**, 222.

[5] Aloy, *Bull. Soc. chim.*, 1900, [3], **23**, 368.

tive to light and have been employed for photographic purposes. The most important are described in the sequel, together with the other uranium salts.

The Uranates.—The alkali uranates are obtained by precipitating a uranic salt with an alkali, those of the alkaline earths and other metals by precipitating a mixture of a uranyl salt and a corresponding metallic salt with ammonia. They are also formed when a mixture of a metallic uranate and the acetate or carbonate of the metal is heated in the air. The uranates generally have the composition $M_2O,2UO_3$, and correspond to the dichromates. They are yellow, insoluble in water but soluble in acids, and are decomposed by heat, like uranic oxide itself.

Potassium Di-uranate, $K_2U_2O_7$.—This is obtained as a pale orange-yellow coloured powder by precipitating a uranyl salt with an excess of potash. Probably the hydroxide is first precipitated and then two molecules unite by the splitting off of water, forming uranic acid, which unites with the excess of alkali to form the potassium salt. It can also be produced by fusing uranyl chloride with potassium chloride and ammonium chloride.

Sodium Di-uranate, $Na_2U_2O_7$, is obtained in a similar manner to the potassium salt, and is known as *uranium yellow*, being used for painting on glass and porcelain, as well as for preparing the yellow glass known as uranium glass. It is prepared on a large scale by roasting 100 parts of pitchblende, containing 45 per cent. of U_3O_8, with 14 parts of lime in a reverberatory furnace. The resulting calcium uranate is treated with dilute sulphuric acid, and the solution of uranic sulphate thus obtained is mixed with sodium carbonate. The uranium is precipitated, together with the other metals, but re-dissolves in an excess of the alkali. On treating this liquid with dilute sulphuric acid, a hydrated sodium uranate, or uranium yellow, $Na_2U_2O_7,6H_2O$, is obtained.[1]

Ammonium Uranate.—This salt sometimes occurs in commerce as a fine deep yellow-coloured precipitate, termed, like the sodium salt, uranium yellow. It is easily obtained by adding ammonium chloride or sulphate to a boiling solution of sodium uranate, washing the resulting precipitate, and drying at a gentle heat. When heated to redness this salt yields pure uranoso-

[1] Patera, *J. pr. Chem.*, 1854, **61**, 397.

uranic oxide, and serves therefore as the raw material for the preparation of other uranium compounds.

Uranoso-uranic Oxide or *Green Oxide of Uranium*, $U_3O_8(=UO_2,2UO_3)$, occurs more or less pure in pitchblende. The pure oxide can be obtained by gently heating the trioxide or the dioxide in the air in the form of a satiny dark-green powder, having a specific gravity of 7·2, and soluble in strong acids. It forms a violet hydroxide which can be prepared by the action of light on a solution of uranyl oxalate or an alcoholic solution of the acetate.[1]

Black Oxide of Uranium or *Uranium Pentoxide*, $U_2O_5(=UO_2,UO_3)$, is formed when the other oxides, or ammonium uranate, are strongly ignited in the air, and when the nitrate is electrolysed. Zimmermann states that it possesses no constant composition.[2]

Uranium Peroxide, UO_4.—When a very dilute solution of hydrogen peroxide is added to one of uranyl nitrate, a yellowish-white precipitate of peruranic hydroxide, $UO_4,4H_2O$ (air dried), is formed, which evolves chlorine when treated with hydrochloric acid.[3] *Peruranates* are formed by the action of alkali and hydrogen peroxide on the uranyl salts (Fairley). Two types of salt are known; in one of these the metal appears to be present as a peroxide and the salt can be hydrolysed by weak acids or bases into a peroxide and uranium peroxide; the hydrolysis of salts of the second type yields uranium peroxide and an ordinary metallic oxide.[4]

Sodium Peruranate, $(Na_2O_2)_2UO_4,8H_2O$, is precipitated when alcohol is added to a solution of uranyl nitrate, caustic potash, and hydrogen peroxide, and crystallises in golden-yellow needle-shaped crystals, which are somewhat more stable than the potassium salt. If the minimum quantity of caustic soda be employed, a red crystalline salt separates out, having the composition $Na_2O_2(UO_4)_2,6H_2O$. A red crystalline salt, Na_2UO_5,H_2O, is formed when peruranic hydroxide is added to hydrogen peroxide containing alcohol. It slowly decomposes with evolution of oxygen.[5] The formation of a salt of this type is the cause of the red coloration produced when hydrogen

[1] See Aloy, *Bull. Soc chim.*, 1900, [3], **23**, 368.

[2] *Annalen*, 1885, **232**, 276.

[3] Fairley, *Journ. Chem. Soc.*, 1877, i., 127.

[4] Melikoff and Pissarjewsky, *Ber.*, 1897, **30**, 2902; *Zeit. anorg. Chem.*, 1898, **18**, 59; Pissarjewsky, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 472.

[5] Aloy, *Bull. Soc. chim.*, 1903, [3], **29**, 292.

peroxide and solid potassium carbonate are added to a uranyl salt.[1]

Lead Peruranate is formed as a double salt with lead uranate, $(PbO)_2UO_4,PbUO_4$, by the action of sodium peruranate on lead acetate. Hydrogen peroxide is liberated in the reaction and the resulting lead salt, when treated with dilute acetic acid, yields lead acetate and peruranic hydroxide, but no hydrogen peroxide (Melikoff and Pissarjewsky). Other salts of the heavy metals are prepared in a similar manner; they are more stable than the corresponding salts of molybdenum and tungsten.

Uranium and the Halogens.

507 *Uranium Tetrafluoride* or *Uranous Fluoride*, UF_4, is obtained in the form of a voluminous green powder, when hydrofluoric acid is added to a solution of uranous chloride. It is insoluble in water and hydrofluoric acid, and when heated in the air it leaves a green residue of oxide. When ignited in hydrogen it loses hydrofluoric acid.[2]

Uranous fluoride forms double salts with the alkali fluorides. Potassium urano-fluoride, KF,UF_4, is obtained by the action of reducing agents, such as formic and oxalic acids under the influence of light, upon the potassium urano-oxyfluoride, described below. It is a green powder, resembling uranous fluoride, insoluble in water and in dilute acids.

The *Hexafluoride* is also known. The reaction between fluorine and uranium is extremely vigorous and the product is mainly the tetrafluoride and small quantities of the hexafluoride UF_6. The hexafluoride is best prepared from the pentachloride cooled in an alcohol and carbon dioxide mixture. It forms glistening, colourless, fuming, monoclinic prisms, which sublime without melting at ordinary temperatures under reduced pressure.[3]

Uranyl Fluoride, UO_2F_2, was obtained by Smithells[4] in two modifications. The α-compound is obtained by carefully heating the tetrafluoride in presence of air as a white crystalline sublimate, which is very hygroscopic and yields a yellow solution; the β-derivative is formed by evaporating a solution of the oxide, U_3O_8, in hydrofluoric acid, when it remains as a yellow

[1] Aloy, *Bull. Soc. chim.*, 1902, [3], **27**, 734.
[2] Carrington Bolton, *Ber. Akad. Wiss. Berlin*, 1866, 299.
[3] Ruff, Zedner, Schiller, and Heinzelmann, *Ber.*, 1909, **42**, 492.
[4] *Journ. Chem. Soc.*, 1883, **43**, 125.

mass. Both combine with potassium fluoride, yielding *potassium urano-oxyfluoride*, $UO_2F_2,3KF$, which is a lemon-yellow crystalline precipitate, and is also formed when an excess of potassium fluoride is added to a solution of uranyl acetate. It is trimorphous (Baker).[1] Corresponding sodium, ammonium, and barium salts are known (Bolton). Hydrogen peroxide converts these salts into deep yellow coloured peroxyfluorides.[2]

Uranous Oxyfluoride, UOF_2, is also formed by the action of hydrofluoric acid on the oxide, U_3O_8, and is deposited as a fine green powder.[3]

Uranium Trichloride, UCl_3, is obtained by heating the tetrachloride in hydrogen,[4] or by the continued reduction of uranyl salts with zinc and hydrochloric acid.[5] It is a reddish-brown powder, and dissolves readily in water, forming a red solution, which gradually becomes green with evolution of hydrogen.

Uranium Tetrachloride or *Uranous Chloride*, UCl_4.—This is produced with vivid incandescence, when chlorine is passed over metallic uranium, and is obtained also by igniting uranium dioxide in hydrogen chloride, and exposing a solution of uranic oxide in hydrochloric acid containing alcohol to sunlight.[6] It is best prepared by passing chlorine over a heated mixture of charcoal and any of the uranium oxides, or over uranium carbide.[7] Some pentachloride is simultaneously formed, and may be removed by heating the product in a current of carbon dioxide. It can also be prepared by passing carbon tetrachloride over U_3O_8 at a red heat.[8] It crystallises in splendid dark-green octahedra, having a metallic lustre, and volatilising at a red heat to form red vapours with the normal specific gravity of 13·3. It is extremely deliquescent, fumes strongly on exposure to the air, and dissolves readily in water, with evolution of heat and formation of a deep emerald-green solution. This, when concentrated in a vacuum, leaves an amorphous deliquescent mass of uranous chloride, but when evaporated by heat it decomposes, yielding a soluble residue, probably consisting of the oxychloride. Solutions of uranous chloride yield with

[1] *Journ. Chem. Soc.*, 1879, **35**, 763.
[2] Lordkipanidzé, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 283.
[3] Giolitti and Agamennone, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 114.
[4] Péligot, *Ann. Chim. Phys.*, 1842, **5**, 20.
[5] Zimmermann, *Annalen*, 1882, **213**, 320.
[6] Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 613.
[7] Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 264.
[8] Colani, *Ann. Chim. Phys.*, 1907, [viii], 12, 59.

alkalis a precipitate of uranous hydroxide. The solution acts as a powerful deoxidising agent, reducing gold and silver salts, and converting ferric chloride into ferrous chloride. It was by the analysis of this chloride that Péligot ascertained that the supposed metal was in reality an oxide.

Uranium tetrachloride combines directly with ammonia, forming the compound $3UCl_4,4NH_3$, and unites with the heated chlorides of potassium, lithium, and the metals of the calcium group, forming green salts, $UCl_4,2M^{I}Cl$ or $UCl_4,M^{II}Cl_2$, which are decomposed by water (Aloy).

Uranium Pentachloride, UCl_5, is obtained by the direct union of the tetrachloride with chlorine. It exists in two distinct forms, according as it is produced slowly or quickly. When the current of chlorine is slow, the uranium pentachloride forms long dark needle-shaped crystals, which reflect light with a green metallic lustre, but are of a splendid ruby-red colour when viewed by transmitted light. If the rate at which the chlorine passes be rapid, the pentachloride is deposited in the form of a light brown mobile powder. The magnificent octahedral crystals of the tetrachloride are always deposited in quantity in that part of the tube nearest the heated mixture, while in the cooler part of the tube the black needle-shaped crystals of the pentachloride are formed, mixed with more or less of the brown powder, which is generally carried a considerable distance along the tube. Both the black crystals and the brown powder are extremely hygroscopic, yielding yellowish-green liquids on exposure to the air for a few minutes, and hissing and giving off fumes of hydrochloric acid when thrown into water. Uranium pentachloride cannot be volatilised without partial decomposition, as when heated, either alone or in an atmosphere of chlorine or carbon dioxide, uranium tetrachloride and free chlorine are formed. This dissociation begins in an atmosphere of carbon dioxide at 120°, and is complete at 235°, when the percentage of chlorine contained in the residue shows that one-fifth of the chlorine has been driven off. The tetrachloride when similarly heated loses no chlorine.[1]

Uranyl Chloride or *Uranium Oxychloride*, UO_2Cl_2, is formed when dry chlorine gas is passed over uranium dioxide at a red heat. The tube then becomes filled with the orange-yellow vapour of this compound, which solidifies to a yellow crystalline mass, and is easily fusible, but not very volatile. When

[1] Roscoe, *Journ. Chem. Soc.*, 1874, 933.

strongly heated in dry air it yields chlorine and the dioxide, which then becomes oxidised.[1]

Uranyl chloride is soluble in water, alcohol, and ether, and its aqueous solution yields on evaporation crystals of the hydrate, UO_2Cl_2,H_2O. This may be obtained in solution by acting upon uranic oxide with hydrochloric acid, or by oxidising a solution of uranous chloride with nitric acid.[2]

Uranyl chloride forms double chlorides with the chlorides of the alkali metals. The ammonium salt, $2NH_4Cl,UO_2Cl_2,2H_2O$, crystallises in rhombohedra from a syrupy solution of the mixed salts. The potassium salt, $2KCl,UO_2Cl_2,2H_2O$, is obtained by dissolving potassium uranate in excess of hydrochloric acid, adding potassium chloride, and evaporating, when large rhombic tablets separate out, which have a yellowish-green colour, and are very soluble.[3] The anhydrous compound can be obtained by passing the vapour of the oxychloride over heated potassium chloride.[4] Uranyl chloride combines also with the hydrochlorides of the organic bases (Greville Williams). Several basic chlorides have been described.[5]

Uranium Tetrabromide, UBr_4, is obtained by heating in an atmosphere of bromine vapour a previously ignited mixture of uranous oxide and six times its weight of starch, or of the green oxide with sugar charcoal.[6] The bromide is deposited in the more strongly-heated portions of the tube in lustrous brown tablets of sp. gr. 4·838 at 21°/4°. The specific gravity of its vapour is 19·5. It loses its lustre and becomes dull yellow on the surface in the presence of even traces of oxygen, fumes in the air, and is very deliquescent.

Uranyl Bromide or *Uranium Oxybromide*, UO_2Br_2, is obtained by treating uranous oxide with bromine and water, or by dissolving uranic oxide in hydrobromic acid. On evaporation yellow needles are deposited, which have a styptic taste and decompose when heated.[7] It has not been obtained in the anhydrous state.

Uranium Tetraiodide, UI_4, described by Rammelsberg, is

[1] Oechsner de Coninck, *Ann. Chim. Phys.*, 1904, [8], **3**, 500.

[2] See Mylius and Dietz, *Ber.*, 1901, **34**, 2774.

[3] See Rimbach, *Ber.*, 1904, **37**, 461.

[4] Aloy, *Bull. Soc. chim.*, 1901, [3], **25**, 153.

[5] Aloy, *Bull. Soc. chim.*, 1899, [3], **21**, 613; Orloff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 375; 1903, **35**, 513.

[6] Richards and Merigold, *Zeit. anorg. Chem.*, 1902, **31**, 250.

[7] See Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1902, **12**, 1025.

obtained by dissolving uranous hydroxide in hydriodic acid. A green solution is thus formed, which decomposes on evaporation. The solid substance is formed as a crystalline sublimate when iodine vapour is passed over uranium at a temperature of 500° in sealed vacuum tubes. It forms black needles melting at 500°, and dissolves in water, giving a green acid solution.[1]

Uranyl Iodide, UO_2I_2, is formed when a slight excess of barium iodide is added to an ethereal solution of the nitrate, and separates in red, deliquescent, unstable crystals.[2]

Uranium and Sulphur.

508 *Uranium Sesquisulphide*, U_2S_3, is prepared by heating UBr_3 in sulphuretted hydrogen, and yields *uranium monosulphide*, US, when heated in hydrogen.[3]

Uranous Sulphide, US, is obtained, according to Péligot, when metallic uranium is heated in sulphur vapour. The mass takes fire and an amorphous greyish-black powder is obtained which becomes crystalline when ignited in absence of air. It may also be formed by passing a carefully dried mixture of hydrogen and sulphur vapour over sodium uranium chloride. The sulphide is thus obtained in small flattened crystals.[4]

Ammonium sulphide always gives a black precipitate of the hydrated sulphide with uranous salts. When exposed to moist air the sulphide gives off hydrogen sulphide and is converted into uranyl sulphide, UO_2S.

Uranyl Sulphide, UO_2S, is precipitated when ammonium sulphide is added to a solution of uranyl nitrate. It oxidises quickly on exposure to air, and dissolves easily in acids and in ammonium carbonate. When heated in the presence of water until all the ammonium sulphide has been driven off, it decomposes into sulphur and the dioxide. If air be excluded the ammonium sulphide acts as a reducing agent, and the residual black powder has the composition U_7O_{10}. Uranyl sulphide is formed in black needle-shaped tetragonal crystals when the green oxide is strongly heated with potassium thiocyanate and sulphur.[5]

[1] Guichard, *Compt. rend.*, 1907, **145**, 921.
[2] Aloy, *Ann. Chim. Phys.*, 1901, [7], **24**, 412.
[3] Alibegoff, *Annalen*, 1886, **233**, 117.
[4] Colani, *Ann. Chim. Phys.*, 1907, [viii], **12**, 59.
[5] Milbauer, *Zeit. anorg. Chem.*, 1904, **42**, 448.

Uranium Red.—When sulphuretted hydrogen is passed into a solution of uranyl nitrate to which about 2·8 molecular proportions of caustic potash have been added, an orange-yellow precipitate is produced which dries to a hard, amorphous, brick-red mass and has the composition $5UO_3,2K_2O,H_2S_2$. When this substance is treated with potassium carbonate or caustic potash it is converted into uranium red, which is a blood-red precipitate and dries to a brittle amorphous mass resembling potassium permanganate in appearance and yielding a carmine-red powder. This compound has not been obtained free from water, but has the composition $5UO_3,2K_2O,HS_2K,xH_2O$, and is converted into the orange-yellow substance by carbonic acid. Acids decompose it with liberation of half the sulphur as free sulphur and half as sulphuretted hydrogen.[1] An analogous ammonium-red can be obtained by the action of ammonium sulphide on uranyl nitrate, and it was in this way that uranium red was first prepared.[2]

The *selenides*, USe_2 and U_2Se_3, and the *telluride*, U_2Te_3, have been obtained in the crystalline state by heating the double chloride, $UCl_4,2NaCl$, in hydrogen containing the vapour of selenium or tellurium.[3] A crystalline *uranyl selenide*, UO_2Se, is obtained by heating the green oxide with potassium cyanide and sulphur.[4]

Uranyl Sulphite.—When sulphur dioxide is passed into a solution of uranyl acetate a crystalline precipitate is produced which has the empirical composition $UO_3,SO_2,4H_2O$ and was regarded by Girard[5] as the normal sulphite, $UO_2,SO_3,4H_2O$. Kohlschütter,[6] however, formulates it as a uranyl sulphurous acid, $SO_3H.UO_2.OH,3H_2O$, and has prepared a number of complex alkali salts.

Uranous Sulphate, $U(SO_4)_2,9H_2O$, crystallises from aqueous solution in greenish monoclinic twinned prisms and is isomorphous with crystallised thorium sulphate.[7] It is, however, usually obtained with $8H_2O$. In order to prepare this salt, the green oxide, U_3O_8, is dissolved in dilute sulphuric acid and the solution allowed to crystallise after addition of

[1] Kohlschütter, *Annalen*, 1900, **314**, 311.

[2] Patera, *J. pr. Chem.*, 1850, **51**, 122; Remelé, *Annalen*, 1865, **125**, 209; Zimmermann, *ibid.*, 1880, **204**, 204.

[3] Colani, *Compt. rend.*, 1903, **137**, 382.

[4] Milbauer, *Zeit. anorg. Chem.*, 1904, **42**, 450.

[5] *Compt. rend.*, 1852, **34**, 22.

[6] *Annalen*, 1900, **311**, 1.

[7] Rammelsberg, *Zeit. Kryst. Min.*, 1889, **15**, 640.

some alcohol. The mother-liquor, which contains uranyl sulphate, yields another crop of crystals of uranous sulphate after it has remained exposed to the light, inasmuch as the uranyl salt present in solution is reduced by the alcohol.

Sodium hyposulphite has also been found a satisfactory reducing agent. Uranous sulphate forms a stable hydrate with $4H_2O$ and several other hydrates, and is readily decomposed by water with formation of basic salts.[1] It forms double salts with the sulphates of the alkali metals;[2] as, for instance, $U(SO_4)_2,K_2SO_4,2H_2O$, and $U(SO_4)_2,(NH_4)_2SO_4,H_2O$.

Uranyl Sulphate, $UO_2SO_4,3H_2O$, is obtained by heating uranyl nitrate with sulphuric acid, and does not crystallise readily. It dissolves in about 20 parts of water at the ordinary temperature.[3] When dissolved in moderately concentrated sulphuric acid, fine yellowish-green fluorescent crystals of UO_2SO_4,H_2SO_4 are deposited on cooling, whilst from a solution in concentrated sulphuric acid crystals of a disulphate, $UO_2S_2O_7$, are deposited, which do not fluoresce. By the gradual oxidation of the pitchblende found in Joachimsthal, several new uranium minerals have been formed. Amongst the more important are certain sulphates, such as uranium-vitriol or johannite, and some basic sulphates.

Uranyl sulphate forms double salts with the sulphates of the alkali metals, such as $UO_2SO_4,K_2SO_4,2H_2O$. This is very soluble, and crystallises in yellow crusts, whilst the sparingly soluble ammonium salt, $UO_2SO_4,(NH_4)_2SO_4,2H_2O$, is deposited in monoclinic lemon-coloured prisms.[4]

Uranium and Nitrogen, Phosphorus, and Arsenic.

509 *Uranium Nitride.*—Uranium combines directly with nitrogen at 1000°, forming a yellow nitride,[5] the composition of which is not stated. The *nitride*, U_3N_4, is obtained as a very

[1] Orloff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 381; Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1901, 483; Kohlschütter, *Ber.*, 1901, **34**, 3628; Giolitti and Bucci, *Gazz.*, 1905, **35**, ii., 151, 162; Giolitti and Liberi, *ibid.*, 1906, **36**, ii., 443.

[2] See Kohlschütter, *Ber.*, 1901, **34**, 3619.

[3] Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1901, 222, 349; 1902, 94, 161.

[4] See also Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1904, 1171; 1905, 50, 94, 151, 182.

[5] Moissan, *Compt. rend.*, 1896, **122**, 274.

stable [1] grey or black powder by heating the tetrachloride in ammonia, mixing the product with ammonium chloride, and again igniting in an atmosphere of ammonia.

Uranyl Nitrate, $UO_2(NO_3)_2,6H_2O$.—This salt, which is commonly known as uranium nitrate, is prepared by dissolving any of the oxides of uranium in nitric acid. It crystallises in fine lemon-yellow fluorescent rhombic prisms, which are soluble in half their weight of water [2] and deliquesce on exposure. The aqueous solution has an acid reaction owing to the partial hydrolysis of the salt.[3] The nitrate is prepared commercially by igniting ammonium uranate, $(NH_4)_2U_2O_7$, and dissolving the oxide in nitric acid.[4] It readily forms double salts with the alkali nitrates.[5]

Uranium phosphide, U_3P_4, *arsenide*, U_3As_4, have been prepared by Colani [6] in a similar manner to the telluride (p. 1117) as black crystalline powders, readily oxidised by nitric acid.

Uranous metaphosphate, $U(PO_3)_4$, *uranous pyrophosphate* UP_2O_7, and *uranous orthophosphate* $U_3(PO_4)_4$, have been prepared by Colani.[7]

Uranyl Phosphates.—The normal orthophosphate is not known. The mono-hydrogen salt, $H(UO_2)PO_4,4H_2O$, is deposited in yellow tetragonal plates from a solution of precipitated uranium phosphate in hot water acidified with hydrochloric acid.[8] When uranic oxide is treated with phosphoric acid, a crystalline powder is obtained which is partially soluble in water, and the solution deposits yellow crystals of the di-hydrogen salt, $UO_2(H_2PO_4)_2,3H_2O$.

Uranyl Ammonium Phosphate, $UO_2NH_4PO_4$, is a greenish-yellow precipitate, insoluble in acetic acid, obtained by adding a soluble phosphate to a solution of uranyl acetate containing ammonium chloride. This reaction is employed for the volumetric estimation of uranium, as well as for that of phosphoric acid.

Uranyl Arsenates.—Several of these compounds exist

[1] Kohlschütter, *Annalen*, 1901, **317**, 158.

[2] See Oechsner de Coninck, *Compt. rend.*, 1900, **131**, 1219, 1303; 1901, **132**, 90, 204; *Bull. Acad. roy. Belg.*, 1901, 222.

[3] Ley, *Zeit. physikal. Chem.*, 1899, **30**, 193; *Ber.*, 1900, **33**, 2658; Dittrich, *Zeit. physikal. Chem.*, 1899, **29**, 449.

[4] Janda, *Oester. Zeit. Berg.-Hütt.*, 1901, **49**, 325.

[5] Meyer and Wendel, *Ber.*, 1903, **36**, 4055; Rimbach, *ibid.*, 1904, **37**, 461.

[6] *Compt. rend.*, 1903, **137**, 382.

[7] *Ann. Chim. Phys.*, 1907, [viii], **12**, 59.

[8] Bourgeois, *Bull. Soc. franç. Min.*, 1898, **21**, 32.

as minerals (Winkler). Trögerite has the composition $(UO_2)_3(AsO_4)_2,12H_2O$; walpurgite is a basic arsenate of uranyl and bismuth; uranospinite is an arsenate of uranium and calcium.

Uranium and Carbon.

510 *Uranium Carbide*, U_2C_3, is obtained by strongly heating a mixture of 500 grams of green uranium oxide and 60 grams of charcoal in the electric furnace, and is a crystalline lustrous solid, which scratches rock crystal but not corundum, and has a specific gravity of 11·28 at 18°. It is attacked by fluorine when gently warmed, by chlorine at 350°, and by oxygen at 370°. In contact with water, about one-third of the carbon is evolved as a gaseous mixture containing 0·2–0·7 per cent. of acetylene, 5·0–7·0 per cent. of ethylene, 78–81 per cent. of methane, and 13·5–15·0 per cent. of hydrogen, the remainder of the carbon being converted into a mixture of solid and liquid hydrocarbons.[1] When two pieces of the carbide are rubbed together, or even shaken in a bottle, brilliant sparks are given off.

Uranyl Carbonates.—Double salts of uranyl carbonate and alkali carbonates are obtained by precipitating a uranyl salt with an alkali carbonate. The potassium salt, $UO_2CO_3,2K_2CO_3$, is obtained by dissolving potassium uranate in potassium bicarbonate, and evaporating at a moderate temperature, when the compound is deposited in silky crystalline crusts.[2] Water dissolves at the ordinary temperature 7 per cent. of its weight of this salt. The corresponding sodium salt is obtained in a similar way, and possesses similar properties. The ammonium compound, $UO_2CO_3,2(NH_4)_2CO_3$, is prepared by gently warming ammonium uranate with a solution of ammonium carbonate, and separates out on cooling in lemon-yellow small flat monoclinic prisms. It dissolves at the ordinary temperature in 20 per cent. of water, but is less soluble in water containing ammonium carbonate. The mineral liebigite is a uranyl calcium carbonate, $UO_2CO_3,CaCO_3,10H_2O$, which occurs as an apple-green warty mass, together with other uranium minerals.

Detection and Estimation of Uranium.

511 The uranous salts are green and pass rapidly by oxidation into the uranyl salts, which have a yellow colour, and yield

[1] Moissan, *Compt. rend.*, 1896, **122**, 274.

[2] See also Oechsner de Coninck, *Bull. Acad. roy. Belg.*, 1904, 363, 448.

with alkalis or alkali carbonates yellow precipitates of the alkali uranates.

In the general separation of the metals uranium is obtained together with iron. In order to separate these, the precipitated oxides are washed and treated with a concentrated solution of ammonium carbonate, and filtered. Uranium is detected in the filtrate after supersaturation with hydrochloric acid, by the brown precipitate produced with ferrocyanide of potassium. When a uranium compound is fused with microcosmic salt in the oxidising flame, a yellow bead is obtained which on cooling becomes green, and on re-heating attains a darker green colour.

Most of the uranyl salts show a strong fluorescence, and give a characteristic absorption spectrum, which has been examined by Morton and Bolton,[1] whilst the fluorescence and phosphorescence spectra have been described by E. Becquerel[2] and H. Becquerel.[3]

The uranium compounds do not impart any tint to the non-luminous gas flame. The spark spectrum of uranium is a complicated one, and has been mapped by Thalén. It consists of a large number of lines, of which five in the green are conspicuous by their brightness, viz. 5495, 5482, 5480, 5478, and 5475; there are also three specially bright lines in the more refrangible portions, viz., 4473, 4363, and 4341.

In order to estimate uranium[4] it is converted into a uranyl salt, precipitated with ammonia, and the washed precipitate converted by ignition into the green oxide. It may, like iron, be estimated volumetrically with a solution of potassium permanganate, the uranyl compound being previously reduced to the uranous salt by the action of zinc and sulphuric acid, or the solution of uranyl acetate may be titrated with sodium phosphate. The hydrated oxide is deposited when solutions of uranyl salts are electrolysed.

The Atomic Weight of uranium was determined by Péligot by the analysis of the tetrachloride, which he found to contain 37·2 per cent. of chlorine, whence he calculated the number 237·6 as the atomic weight. He afterwards obtained the number 238·3

[1] *American Chemist*, **3**, 360, 401; see also Vogel, *Ber.*, 1875, **8**, 1535; 1878, **11**, 915; Zimmermann, *Annalen*, 1882, **213**, 285.

[2] *Compt. rend.*, 1872, **75**; 1879, **88**, 1237.

[3] *Compt. rend.*, 1885, **101**, 1252; 1907, **144**, 459.

[4] A summary of the best methods of estimation is given by Kern, *J. Amer. Chem. Soc.*, 1901, **23**, 685.

by the conversion of the acetate, $UO_2(C_2H_3O_2)_2,H_2O$, into the dioxide. Zimmermann, on the other hand, by the same method, obtained the number 237·7, whilst from a series of experiments in which he converted the dioxide into the green oxide and *vice versâ* the number 237·8 was found.[1] Aloy,[2] by the determination of the ratio $UO_2:N$ in pure uranyl nitrate, obtained the value 237·6 (N = 13·93), which becomes 237·1 when the more modern value N = 13·90 is adopted. Richards and Merigold,[3] by analysis of the very carefully purified tribromide, obtained the value 238·5, whilst Lebeau[4] found the same number by the reduction of uranyl nitrate dihydrate to uranium oxide by heating the salt in a current of hydrogen to 1100°. Hence the number 238·5 is now adopted. (1913)

GROUP VII.

Sub-group (a)	*Sub-group (b)*
Fluorine.	Chlorine.
Manganese.	Bromine.
	Iodine.

512 In the periodic system, manganese is the only metallic representative of the even series of the seventh group as yet known, the typical elements of which are fluorine and chlorine, and the remaining members bromine and iodine.

The halogen elements have already been described in Vol. I. The analogy of manganese with these elements is almost entirely confined to the derivatives of its highest oxide, Mn_2O_7. To this oxide corresponds permanganic acid, $HMnO_4$, the salts of which are isomorphous with the perchlorates.

In its general chemical behaviour, however, manganese shows strong resemblances to both chromium and iron, between which it stands in the fourth horizontal series. Like chromium, it forms a basic oxide, R_2O_3, a dioxide, RO_2, and an acidic trioxide, RO_3, and the potassium salt of the acid corresponding to the latter crystallises in the same forms as potassium sulphate and chromate. Both this oxide and the salts are, however, much less stable than the corresponding chromium compounds. On the other hand, manganese resembles iron in forming three

[1] *Annalen*, 1885, **213**, 299.
[2] *Compt. rend.*, 1901, **132**, 551.
[3] *Zeit. anorg. Chem.*, 1902, **31**, 235.
[4] *Compt rend.*, 1912, **155**, 163.

oxides of the types RO, R_2O_3, R_3O_4, and both iron and chromium in forming two series of salts corresponding to the first two of these. The manganic salts are, however, very unstable, whilst the manganous salts are much more permanent than the divalent salts of iron or chromium.

MANGANESE. Mn = 54·93.

513 Black oxide of manganese, manganese dioxide, or pyrolusite was known in early times, but for a long period this compound was confounded with magnetic iron ore, and this fact explains the statement of Pliny that loadstone was employed in the manufacture of glass for the purpose of removing or attracting the impurities of colouring matters out of the glass. He distinguished, moreover, special kinds of magnes; one of these, which is of the feminine gender, does not attract iron: "magnes qui niger est et feminei sexus, ideoque sine viribus." This probably was manganese dioxide. The derivation of the word magnet appears to be doubtful. In the Middle Ages loadstone was distinguished as *magnes* or *magnesius lapis*. Pyrolusite, however, was termed *magnesia* probably because Pliny had already pointed out the existence of two species of loadstone. Many of the alchemists, however, believed it to be an ore of iron. They likewise mention its use in glass-making, and in the Latin manuscripts of the sixteenth century it is designated by the term *lapis manganensis*, or similar names.

In 1740, Pott, in his treatise entitled "*Examen chymicum magnesia vitrariorum, Germanis Braunstein*," proved that the black oxide of manganese did not contain iron, and that from it a definite series of salts could be obtained. He did not, however, suggest that it contained a new metal. Scheele's celebrated investigations on manganese were published in the year 1774. In these he showed that the mineral manganese possesses a strong attraction for phlogiston, and that it takes this substance up, uniting with acids to form colourless salts; this being explained, according to our present views, by the fact that it gives off oxygen. On the other hand, the solutions of manganese which did not contain phlogiston were shown to be coloured. Scheele believed that the earth contained in this mineral resembled lime; but in the above-mentioned

year Bergman, founding his deductions upon Scheele's experiments, came to the conclusion that manganese was probably the calx of a new metal, inasmuch as it coloured glass, and its solutions were precipitated by prussiate of potash, these being reactions common to the metallic calces. Gahn was, however, the first to isolate the new metal. In Germany this was called Braunstein-könig or Braunstein-metal. In other languages, in which Braunstein was termed *magnesia niger*, in order to distinguish it from *magnesia alba*, the metal was called manganese or manganesium.

Manganese occurs in nature chiefly as the dioxide or pyrolusite, MnO_2. It is found also in the following minerals; braunite, Mn_2O_3; hausmannite, Mn_3O_4; psilomelane, $(Mn,Ba)O,MnO_2$; manganite, Mn_2O_3,H_2O; rhodocrosite or manganese spar, $MnCO_3$, which also frequently occurs as an isomorphous constituent in ferrous carbonate and other similar minerals. Manganese occurs also as alabandite or sulphide of manganese MnS; and hauerite, or manganese disulphide, MnS_2. It likewise forms an essential constituent of many other minerals, although occurring in them only in small quantity. Thus, for instance, most silicates contain manganese, which frequently imparts to them their peculiar colour. By means of these minerals the metal manganese passes into the soil and into drainage water, whence it is absorbed in small quantities into the bodies of plants and animals.

The natural oxides of manganese usually contain traces of potassium, rubidium, silver, and copper, whilst gallium, indium, and thallium are occasionally present.[1]

514 *Preparation of Metallic Manganese.*—The higher oxides of manganese can be reduced only to manganese monoxide at a red heat, the metal not being formed either when the oxide is heated alone or mixed with charcoal in a current of hydrogen until the temperature rises to white heat. The original method of preparing the metal, proposed by John,[2] depends upon this fact. Finely divided oxide of manganese, obtained by the calcination of the carbonate in a covered crucible, is well mixed with carbon, and the mixture formed into a paste with oil; the paste is then introduced into a crucible lined with charcoal, and the upper portion completely filled with powdered charcoal. The crucible is first heated to redness for half-an-hour to solidify the

[1] Hartley and Ramage, *Journ. Chem. Soc.*, 1897, **71**, 533.
[2] Gehlen's *Journ. Chem. Phys.*, **3**, 452.

mass, after which the cover is carefully luted down, and the whole exposed to a wind furnace for an hour-and-a-half to the highest temperature which the crucible can support without fusing. The regulus thus prepared contains both carbon and silicon derived from the ashes of the wood charcoal. By igniting the metal a second time in a charcoal crucible with some borax it was obtained by John in a more fusible and brilliant state, and so free from carbon that it left no black residue when treated with an acid.

Deville's method [1] consists in mixing red manganese oxide Mn_3O_4, prepared by heating the artificial dioxide, with sugar charcoal insufficient in quantity for complete reduction. The mixture is placed in a doubly-lined crucible and heated to whiteness. The regulus obtained is coated with a violet crystalline mass which appears to be calcium-manganese spinel, CaO,Mn_2O_3.

Hugo Tamm [2] suggests the following as the best method of preparation on the large scale. A flux is prepared of twenty parts of powdered soda-lime glass and seven parts of fluor-spar; six parts of this mixture are then added to one part of lampblack and eleven parts of powdered black oxide of manganese. The mass is heated in a plumbago crucible which has been lined with a mixture of three parts of graphite and one part of fire-clay, and this is then intensely ignited in a wind furnace. A green slag termed "green flux" is obtained in this operation, together with metallic manganese, and this flux serves for a fresh operation. Seven parts of this flux are mixed with ten parts of the best manganese dioxide, one part of lampblack, and some oil. The mass is brought into a similar crucible, covered with a thick piece of wood, and the cover luted down, a small opening being left for the escape of the gases which are evolved. It is first heated gently, and then ignited at a white heat for several hours. In this way four parts are obtained of impure manganese metal, which is found to be covered with a grey slag; the latter may be employed for further smelting operations, especially if some of the first flux be added.

This impure manganese, termed cast manganese, contains a variety of impurities. A specimen of pyrolusite containing 50·5 per cent. of manganese and 3·5 per cent. of iron gave a regulus having the composition given in column I.; after fusion

[1] *Ann. Chim. Phys.*, 1856, [3], **46**, 182.
[2] *Chem. News*, 1872, **26**, 111.

with half its weight of manganese carbonate this regulus yielded a product possessing the composition given in column II.

	I.	II.
Manganese	96·90	99·910
Iron	1·05	0·050
Silicon	0·85	0·015
Carbon	0·95	0·025
Aluminium	0·10	—
Calcium	0·05	—
Phosphorus	0·05	—
Sulphur	0·05	—
	100·000	100·000

Jordan [1] describes a method of preparing metallic manganese on a large scale by treating manganese ores in a blast furnace. The metal obtained is cast manganese, containing 85 per cent. of manganese, 6 per cent. of carbon, 8 per cent. of iron, and traces of silicon, sulphur, and phosphorus.

Other processes of preparing the metal consist in igniting a mixture of fluor-spar and chloride of manganese with metallic sodium,[2] or gradually adding 15 gr. of metallic magnesium to a fused mixture of 100 gr. of manganese chloride and 200 gr. of potassium chloride.[3] The metal may be obtained also by the electrolysis of a concentrated solution of the chloride according to the process described by Bunsen,[4] or by heating the amalgam, which can be prepared electrolytically.[5]

The method of reducing manganese oxide by aluminium is due to Greene and Wahl,[6] who devised it for producing the pure metal cheaply. The metal they obtained contained 96·5 per cent. of manganese, 2·0 per cent. of iron, and 1·5 per cent. of silicon.

In recent years a considerable amount of metallic manganese has been made by the Goldschmidt process (see Aluminium), and this attains a high degree of purity, containing as much as 98·5 to 99·0 per cent. of the metal. Lebeau [7] has, however, shown that metal so produced may contain as much as 5·25 per cent. of silicon.

[1] *Compt. rend.*, 1878, **86**, 1374.
[2] Brunner, *Pogg. Ann.*, 1857, **101**, 264.
[3] Glatzel, *Ber.*, 1889, **22**, 2857.
[4] *Pogg. Ann.*, 1854, **91**, 619.
[5] Prelinger, *Monatsh.*, 1894, **14**, 353.
[6] *Trans. American Institute of Mining Engineers*, 1893, **21**, 887.
[7] *Ann. Chim. Phys.*, 1904, **1**, **553**.

With regard to the preparation of manganese in the electric furnace,[1] Moissan proved that by using excess of oxide, the reduced metal might be obtained free from carbon and silicon. This method has recently been put into commercial use, but the efficiency of the process is not such as to yield metal at a low cost, for Moissan has shown that manganese is highly volatile at electric furnace temperatures, and that as much as 400 grammes of the metal may be volatilised in ten minutes in the electric arc.

Manganese has been obtained also by electrolysis. Ferro-manganese anodes are allowed to dip into fused sodium chloride, and an electric current is passed. Pure manganese is deposited at the cathode.[2] It has been prepared also by electrolysing manganese dioxide dissolved in fused fluorspar.[3]

Properties.—Pure manganese, obtained by the reduction process, is a grey or reddish-white metal, having the colour and appearance of cast iron. It is very hard and brittle, has a specific gravity of about 8·0, and oxidises so easily in the air that it must be kept under rock-oil or in well-sealed vessels. Cast manganese containing iron is, however, unalterable in the air. Manganese is readily dissolved by all dilute acids, yields sulphur dioxide with hot concentrated sulphuric acid,[4] and decomposes water with evolution of hydrogen even in the cold, more rapidly when heated. It melts[5] at 1245°, volatilises readily at the temperature of the electric furnace, being more volatile than nickel, chromium, or iron.[6] Manganese combines rapidly with nitrogen above 1210°.

Alloys of Manganese.

515 The alloys of manganese and copper closely resemble those of tin and copper.[7] Those which contain from 5 to 8 per cent. of manganese are malleable, but those in which a higher percentage of manganese is present become grey and brittle.

Manganese bronze is made by adding cupro-manganese containing about 25 per cent. of manganese to the molten bronze. For industrial purposes it contains from 1 to 3

[1] *Compt. rend.*, 1892, **116**, 1429. [2] D. R. P., 74959.
[3] Eng. Patent, 17190. [4] Adie, *Proc. Chem. Soc.*, 1899, **15**, 133.
[5] Heraeus, *Zeit. Elektrochem.*, 1902, **8**, 185.
[6] Moissan, *Compt. rend.*, 1906, **142**, 425.
[7] Valenciennes, *Compt. rend.*, 1870, **70**, 607.

per cent. of manganese, 8 to 15 per cent. of tin, and 0 to 5 per cent. of zinc, the rest being copper.

The alloys of manganese, copper, and zinc of most commercial value contain from 58 to 60 per cent. of copper, from traces to 2·2 per cent. of manganese, and from 39 to 41 per cent. of zinc; they closely resemble German silver, and may serve as a substitute for this substance.

Alloys of manganese with aluminium, antimony, tin, bismuth, arsenic, and boron are noteworthy owing to the remarkable magnetic properties which they possess.[1]

The alloys of manganese and iron, such as manganese steels, spiegeleisen, ferromanganese, and silico-spiegel, will be described under iron.

Manganese Amalgam is prepared by electrolysing a saturated solution of manganous chloride, mercury being used as the negative pole. When the pasty mass which is obtained is strained and strongly compressed, it yields a slate-coloured mass of specific gravity 12·828, which has the composition Hg_5Mn_2 (Prelinger).

COMPOUNDS OF MANGANESE.

Manganese and Oxygen.

516 Manganese forms a series of oxides, of which the following are the best defined:

Manganese monoxide, MnO,
Trimanganese tetroxide, Mn_3O_4,
Manganese sesquioxide, Mn_2O_3,
Manganese dioxide, MnO_2,
Manganese trioxide, MnO_3,
Manganese heptoxide, Mn_2O_7.

The first of these is a powerful basic oxide, whilst the sesquioxide is feebly basic, giving rise to an unstable series of salts, and the oxide, Mn_3O_4, behaves in many respects as a compound of the two. The dioxide acts as a weak acidic oxide, yielding salts known as the manganites with strong bases. Manganese trioxide and the heptoxide are well-marked acid-forming oxides. The manganates, derived from manganic acid, H_2MnO_4, are very unstable, and as already mentioned are iso-

[1] Hogg, *Brit. Assoc. Reports*, 1892, 671; Heusler, *Ber. deut. physikal. Ges.*, 1903, 5. 220,

morphous with the sulphates and chromates. Permanganic acid, $HMnO_4$, is a strong acid and yields stable salts, which are isomorphous with the perchlorates. The substance described by Franke as the tetroxide, MnO_4, does not appear to exist (Thorpe and Hambly).

Manganese Monoxide, or *Manganous Oxide*, MnO, is best prepared by fusing together a mixture of equal parts of anhydrous manganese chloride and sodium carbonate, to which some ammonium chloride has been added, and lixiviating the fused mass with water.[1] It is obtained also when a higher oxide or the carbonate is ignited in a current of hydrogen. Manganous oxide is a greyish-green powder, which fuses at a white heat without loss of oxygen. It has a specific gravity of 5·09. When the powdered oxide is heated in an atmosphere of hydrogen containing a very small quantity of hydrogen chloride it is obtained crystallised in transparent regular octahedra of an emerald-green colour and an adamantine lustre.[2] It has been found in Sweden as the crystalline mineral manganosite.

Manganous Hydroxide, $Mn(OH)_2$, is obtained as a white precipitate when caustic alkali is added to the solution of a manganese salt. As it oxidises rapidly in the air and assumes a brown colour, forming the oxide Mn_3O_4 and finally Mn_2O_3, it must be precipitated in an atmosphere free from oxygen, and dried at a moderate heat in a current of hydrogen. The powder thus obtained is frequently pyrophoric, and when touched with a piece of red-hot charcoal it begins to glow at the point of contact, the oxidation proceeding rapidly throughout the mass. It occurs in Sweden as the mineral pyrochroïte.

When ammonia is added to a solution of a manganous salt containing an ammonium salt, no immediate precipitation occurs, but on standing a precipitate separates out which consists of manganous hydroxide, if air be excluded, but of a brown hydrated oxide in the presence of air. When manganous hydroxide is treated with an ammonium salt it dissolves to an extent which is directly proportional to the concentration of ammonium ions in the solution, and it seems probable that complex ions containing ammonium and manganese are formed.[3]

[1] Liebig and Wöhler, *Pogg. Ann.*, 1830, **21**, 584.
[2] Deville, *Compt. rend.*, 1861, 53, 199.
[3] Herz, *Zeit. anorg. Chem.*, 1899, **21**, 243; **22**, 279.

The manganous salts, MnR^{I}_{2}, are usually faintly pink-coloured, although, according to some chemists, this coloration is due to the presence of a trace of a manganic compound. The halogen salts, as well as the nitrate and sulphate, are readily soluble in water.

Mangano-Manganic Oxide, Red Oxide of Manganese, or *Tri-manganese Tetroxide*, Mn_3O_4, occurs with other manganese ores, and also by itself as the mineral hausmannite. This mineral crystallises in acute tetragonal pyramids, and one of its best localities is Ilmenau in Thuringia. Its specific gravity is 4·85. If manganese monoxide is heated in contact with air, or if the higher oxides are strongly heated either in contact or out of contact with air, this same compound is obtained in the form of a brownish-red powder, which then has a specific gravity of 4·72, and is converted into crystals of hausmannite by being gently heated in a slow current of hydrogen chloride.[1] It is obtained in the crystalline form also by heating a mixture of manganese sulphate and potassium sulphate to bright redness,[2] or by treating a mixture of manganous oxide and calcium chloride in the same way.[3] This oxide dissolves in cold concentrated sulphuric acid, giving rise to a red solution containing a mixture of manganous and manganic sulphates, whilst acetic acid dissolves one-third of the manganese as manganous acetate and leaves the remainder in the form of the sesquioxide.[4] Hence the red oxide is often considered to be a compound having the formula MnO,Mn_2O_3 or $2MnO,MnO_2$. Thus in many respects it behaves in a similar way to the red oxide of lead; on heating with dilute sulphuric acid, for example, manganous sulphate and manganese dioxide are formed, and boiling nitric acid decomposes it in a manner similar to that in which it acts on red lead;

$$Mn_3O_4 + 4HNO_3 = 2Mn(NO_3)_2 + MnO_2 + 2H_2O.$$

Chlorine gas is given off when this oxide is heated with hydrochloric acid, and manganous chloride is formed:

$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$

Mixed oxides of the type Mn_2O_3,RO, which appear to be

[1] Deville, *Compt. rend.*, 1861, **53**, 199.
[2] Debray, *Compt. rend.*, 1861, **52**, 985.
[3] Kuhlmann, *Compt. rend.*, 1861, **52**, 1283.
[4] Gorgeu, *Bull. Soc. chim.*, 1903, [3], **29**, 1111, 1167.

isomorphous with hausmannite (Gorgeu), have been prepared by fusing the corresponding sulphates and by the ignition of the metallic manganites.

Manganic Oxide or *Manganese Sesquioxide*, Mn_2O_3.—This oxide occurs as the mineral braunite crystallised in obtuse tetragonal pyramids. It possesses a sub-metallic lustre, has a dark brownish-black colour, and a specific gravity of 4·75. It may be obtained artificially by igniting any of the oxides of manganese in oxygen or in a mixture of this gas and nitrogen which does not contain more than twenty-six per cent. of oxygen.[1] It then forms a black powder, having a specific gravity of 4·32.

Manganic Hydroxide, MnO(OH), occurs in nature as manganite in steel-grey or arsenic-black crystals, belonging to the tetragonal system, and having a specific gravity of 4·3. It is usually accompanied by other manganese ores, together with a calc-spar and heavy-spar. In general appearance it closely resembles pyrolusite (manganese dioxide), but it may be distinguished from this compound by its giving a brown instead of a black streak when rubbed on an unglazed porcelain plate. When the mineral is heated at 270–310° in the air it is converted without change of form into the dioxide.[2] Manganic hydroxide is formed when manganous hydroxide is allowed to oxidise in moist air. It may be prepared also by passing chlorine into water in which an excess of manganese carbonate is suspended, or by decomposing the corresponding manganic sulphate with water (Carius).[3] It forms a dark-brown powder capable of soiling very strongly and gives off its water at a temperature above 100°. It dissolves in hot nitric acid with formation of manganous nitrate and manganese dioxide:

$$2MnO(OH)+2HNO_3=Mn(NO_3)_2+MnO_2+2H_2O.$$

From this reaction it would appear that in constitution this body resembles lead sesquioxide and analogous compounds, having the constitution MnO,MnO_2, but in other reactions it acts as a feebly basic oxide, whose salts with a few exceptions, are very unstable.

The manganic salts, MnR^{I}_3 or $Mn_2R^{II}_3$, are extremely unstable and are strongly coloured substances. Only the fluoride, sulphate,

[1] Dittmar, *Journ. Chem. Soc.*, 1864, 294.
[2] Gorgeu, *Compt. rend.*, 1888, **106**, 1101.
[3] *Annalen*, 1856, **98**, 53.

and a few derivatives of phosphoric acid have been isolated. The sulphate can replace aluminium sulphate in the alums.

Manganese Dioxide and the Manganites.

517 *Manganese Dioxide, Manganese Peroxide,* or *Black Oxide of Manganese,* MnO_2, is the most important ore of manganese. It occurs in rhombic crystals and in crystalline and amorphous masses, being known to the mineralogist as pyrolusite. It possesses a metallic lustre, an iron-black or dark steel-grey colour, and a black streak. It is opaque and rather brittle, and has a specific gravity of 4·82. The most celebrated localities for this mineral are Ilmenau in Thuringia, near Platten in Bohemia, near Mährisch-Trubau in Moravia, on the Lahn, and in the Caucasus, France, Spain, and North America. It occurs in the United States, abundantly at Vermont, and in Red Island Bay at San Francisco; and also in New Brunswick and Nova Scotia; large quantities too are found in India. It is likewise found in Devonshire. Pyrolusite seldom occurs in the pure state, being generally mixed with other manganese ores such as psilomelane, $(Mn,Ba)O,2MnO_2$, and manganite. It almost always contains ferric oxide, silica, lime, carbonic acid, and traces of the oxides of cobalt and nickel. Pure manganese dioxide is obtained artificially by melting about 600 grms. of the crystallised nitrate and warming until red fumes appear; the clear liquid is then decanted from the lower oxides which first separate out, and is heated in another vessel at 150–160° for 40–60 hours.[1] If manganous carbonate is heated to 260° in presence of air, and the residue is then treated with very dilute cold hydrochloric acid, pure manganese dioxide remains behind (Forchhammer).

A brown precipitate approximating in composition to hydrated manganese dioxide can be obtained from the manganous salts by the aid of a large number of oxidising agents such as potassium permanganate (p. 1143), sodium hypochlorite, ammonia and bromine, nitric acid and sodium chlorate, ammonium persulphate and sulphuric acid,[2] and ozone.[3]

It appears to be almost impossible to prepare perfectly pure hydrated manganese peroxide,[4] since this substance very readily

[1] Gorgeu, *Bull. Soc. chim.*, 1890, [3], **4**, 16.
[2] Marshall, *Journ. Chem. Soc.*, 1891, **59**, 771.
[3] Jannasch and Gottschalk, *Ber.*, 1904, **37**, 3111.
[4] Gorgeu, *Compt. rend.*, 1890, **110**, 1134.

loses a portion of its oxygen, forming mixtures of the composition $xMnO+yMnO_2$, and moreover readily combines with bases forming manganites. Products of constant composition appear to be obtainable only from solutions acidified with a mineral acid.[1] Thus the oxide formed by the reduction of permanganic acid by manganese sulphate, and by the decomposition of permanganic acid in presence of hydrated manganese dioxide, varies in composition from $5MnO_2+MnO$ to $15MnO_2+MnO$. On the other hand, the oxide precipitated from manganous sulphate by dilute potassium permanganate at 80° in presence of zinc sulphate contains all the manganese in the form of dioxide, but combined with alkali. The oxide precipitated from manganese nitrate by nitric acid and sodium chlorate contains 98 per cent. of the manganese as dioxide,[2] and that obtained with ammonium persulphate also contains less than the theoretical amount of oxygen.[3] A similar oxide may also be prepared by treating manganic hydroxide with hot nitric acid,[4] or by adding potassium permanganate to sodium thiosulphate solution. The hydroxide thus obtained, after washing with water, is soluble in water, yielding a brown solution to which the name of manganous acid has been given. This solution turns blue litmus paper red, and does not undergo alteration on standing for many weeks, but small quantities of acid or alkali produce an instant precipitation. Manganese dioxide, like lead dioxide, possesses at the same time feebly basic and feebly acid properties.

Manganese dioxide has long been used for the preparation of colourless glass, and hence pyrolusite has been known as *savon des verriers*. Its mineralogical name, indeed, has reference to this employment of the mineral (from πῦρ, fire, and λύω, I wash). It serves also for the preparation of the manganese compounds and of oxygen, but by far the largest quantity of the mineral is employed for making chlorine, used in the manufacture of bleaching powder.

The Manganites.—Manganese dioxide combines with several basic oxides to form compounds which may be considered as salts of manganous acid. The composition of these compounds seems to depend on the amount of alkali which is present. A large

[1] Rupp, *Zeit. anal. Chem.*, 1903, **42**, 732.
[2] Gooch and Austin, *Amer. J. Sci.*, 1898, [4], **5**, 260.
[3] von Knorre, *Zeit. angew. Chem.*, 1901, **14**, 1149.
[4] Gorgeu, *Ann. Chim. Phys.*, 1862, [3], **66**, 155.

number of them have been described. *Potassium Manganite*, $K_2Mn_5O_{11}$, is obtained as a yellow precipitate when carbon dioxide is passed into a solution of potassium manganate, K_2MnO_4. *Calcium Manganite*, $CaMn_5O_{11}$, is a blackish-brown precipitate formed when a solution of manganous nitrate is poured into an excess of bleaching powder solution.

518 *Regeneration of Manganese Dioxide from the Chlorine Residues.*—Before the year 1856 the whole of the manganese chloride obtained in the manufacture of chlorine from manganese dioxide and hydrochloric acid was allowed to run to waste. In 1821 Forchhammer[1] observed that when manganous carbonate is heated to 260° in an open vessel it is converted into dioxide. Charles Dunlop[2] applied this reaction to the regeneration of manganese dioxide from the chlorine still liquors, the manganous carbonate being prepared by heating manganous chloride solution with calcium carbonate under pressure. In 1857 this process was adopted by Messrs. Charles Tennant and Co., at St. Rollox, but the process has not been adopted elsewhere.

A much less troublesome process was invented by Walter Weldon, in 1867, and first practically carried out at Messrs. Gamble's works at St. Helens, in 1868; it is now universally adopted both by British and Continental manufacturers.

The crude manganese chloride solution remaining in the stills I (Figs. 185–186), which are fitted for using native manganese dioxide, is run into the well K and treated with limestone dust, which neutralises the residual free hydrochloric acid, precipitates the sulphuric acid present as impurity in the hydrochloric acid in the form of calcium sulphate, and then precipitates the ferric chloride as ferric hydroxide; the muddy liquor is thrown by the pump L into the settling tanks A, from which the clear manganous chloride solution is run into the oxidiser B, while the sediment is run into the shute H and so to the drains. In the agitator E lime is slaked to form a thick cream which is run through a sieve into the store and measuring tank F, whence it is charged as required by the pump M into the oxidiser B.

If exactly the theoretical amount of milk of lime be added according to the equation:

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2,$$

it is found that the whole of the manganese is not precipitated

[1] *Ann. Phil.*, 1808, **17**, 50.

[2] *Report of Patent Inventions*, March, 1856, p. 236.

and the mixture absorbs oxygen exceedingly slowly, only half the manganese being converted into dioxide; by adding ten

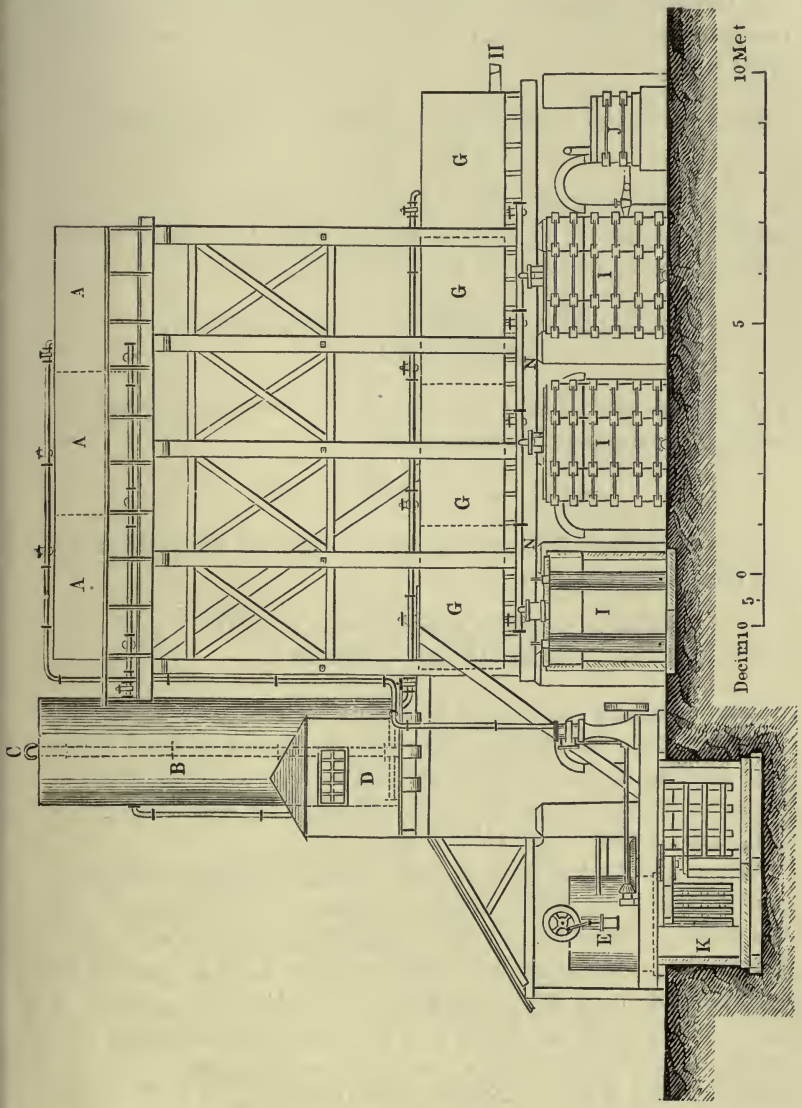


FIG. 185.

per cent. more lime the liquor becomes free from manganese, but the most rapid absorption of oxygen and the most readily settling mud are obtained only by employing about sixty per

cent. more lime (Weldon). When air is pumped by the pipe C through this mixture at 55° C., the alkalinity decreases and disappears owing to the formation of calcium manganite, CaO,MnO_2, and the acid manganite, $CaO,2MnO_2$, whilst a portion of the manganous oxide is converted into manganous manganite, MnO,MnO_2:

$$100MnO + 60CaO + 8O = 12(CaO,2MnO_2) + 48(CaO,MnO_2) + 14(MnO,MnO_2),$$

at about which stage the oxidation practically ceases. An additional quantity of the manganous chloride is next added, which instantly reacts with the CaO,MnO_2, thus:

$$48(CaO,MnO_2) + 24MnCl_2 = 24(CaO,2MnO_2) + 24MnO + 24CaCl_2,$$

and the blowing being continued, the manganous oxide is oxidised to manganous manganite:

$$24MnO + 12O = 12(MnO,MnO_2).$$

Thus the effect of the whole operation may be summarised by the equation:

$$124MnCl_2 + 160CaO + 98O = 36(CaO,2MnO_2) + 26(MnO,MnO_2) + 124CaCl_2.$$

The resulting thin mud is run from the bottom of the oxidising tower by the pipe shown in the figures into one of the four settling tanks G, from which the clear calcium chloride liquor is drawn off by the swivel pipe H into the trough H (Fig. 186), and thence to the drains.

When the plant is stocked with manganous chloride solution and Weldon mud the treatment of native ore is suspended and the chlorine made entirely from the mud, and as this, unlike the native ores, contains no iron which requires to be eliminated by precipitation with limestone dust, it now becomes possible to avoid the use of the latter and to utilise the excess of acid which is invariably left in the chlorine still, even when the artificial mud is used. But as crude hydrochloric acid always contains sulphuric acid, which was eliminated as calcium sulphate in the mud run off from the settling tanks A in the process so far described, it is necessary to provide a new outlet for this impurity, and this is done by treating the hydrochloric

acid with a portion of the waste calcium chloride liquor, the calcium sulphate formed being separated by a sand filter. The purified acid is then used to generate chlorine in the stone stills I, with thick manganese mud run from the settlers G by

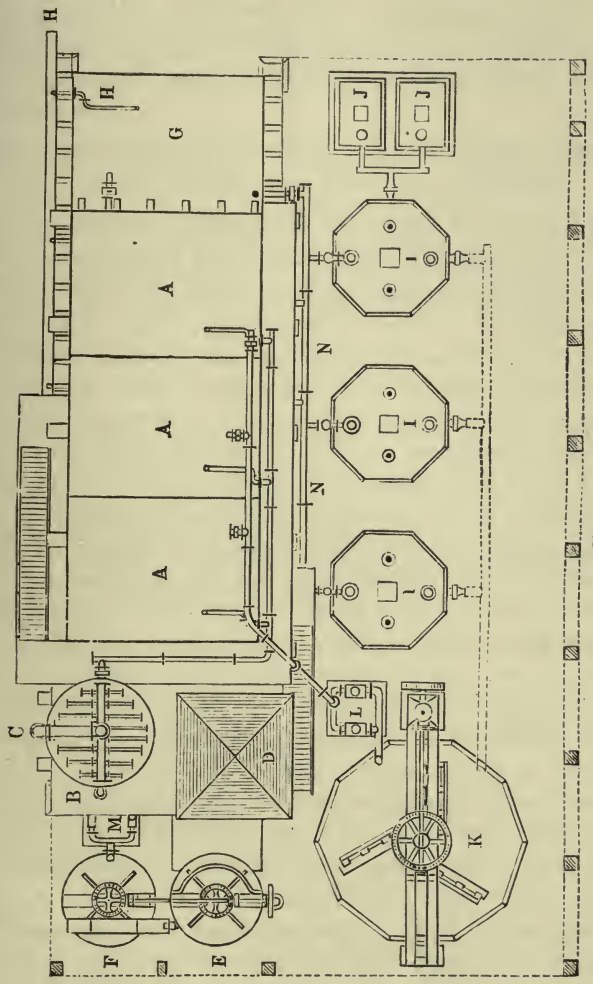


FIG. 186.

the pipe N. When no more chlorine is evolved the residual liquor is treated with an excess of mud more than enough to neutralise all the residual free acid, amounting to about 0·7 per cent. on the liquor; the mixture is then allowed to settle, and the much richer manganese mud settling out forms part of

the next batch to be treated with acid, the reaction being approximately:

$$36(CaO,2MnO_2)+18HCl=18MnO_2+27(CaO,2MnO_2)+9CaCl_2+9H_2O.$$

The Weldon operation thus converts $124MnCl_2$ into $98MnO_2+26MnO$; the equations given above are intended to express the average results obtained.[1]

Manganese Trioxide and Heptoxide, Manganic Acid, Permanganic Acid, and their Salts.

519 In his work entitled *The Prosperity of Germany*,[2] published in 1656, Glauber mentions that when manganese is fused with fixed saltpetre (caustic potash) a mass is produced from which he obtained "a most dainty purple fiery liquor," this afterwards turning blue, red, and green. In 1705 an anonymous treatise appeared, entitled *Key to the Secret Cabinet of Nature's Treasury*; in this it is stated that the product obtained by fusing saltpetre and manganese yields a solution of which the colour alters, first being grass-green, then sky-blue, violet-coloured, and lastly rose-red. The changes of colour which are here given are exactly the opposite of those which Glauber noticed. Pott in 1740 described these changes, believing that they had not been previously noticed, and Scheele, who endeavoured to explain these phenomena, gave to the colouring material the name of mineral chameleon, a term which had previously been applied to other mineral colouring matters capable of undergoing changes of tint. The properties of this mineral chameleon were afterwards investigated by many chemists, but it was not until the year 1817, when Chevillot and Edwards[3] investigated the subject, that a rational view of its composition was arrived at. They showed that when much alkali is employed a green compound is formed; that when, on the other hand, an excess of manganese is fused with potash a red body is produced, and they succeeded in preparing the substance obtained by the latter reaction in the crystalline form. They also showed that an absorption of oxygen takes place, and consequently they assumed that the potash salt forms with a manganate manganese, and that the

[1] A detailed description is to be found in Lunge's *Sulphuric Acid and Alkali Manufacture*, Vol. 3.

[2] Packe's translation, 1687, p. 353.

[3] *Ann. Chim. Phys.*, 1817, [2], 4, 287.

green salt contains more base than the red. Forchhammer[1] investigated the subject in 1820, and ascribed the difference in colour to the existence of two distinct acids. It is, however, to Mitscherlich[2] that we owe a knowledge of the exact composition of these two acids.

Manganese Trioxide, MnO_3, is a deliquescent amorphous reddish mass, prepared by dropping a solution of potassium permanganate in concentrated sulphuric acid on to dry sodium carbonate:[3]

$$2(MnO_3)_2SO_4 + 2Na_2CO_3 = 2Na_2SO_4 + 4MnO_3 + 2CO_2 + O_2.$$

It is formed only in extremely small quantity, and is carried forward by the carbon dioxide as a pink fume, which may be caught on fragments of glass placed in a freezing mixture.

When thrown into water it is decomposed as follows (Thorpe and Hambly):[4]

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

The *manganates* have a green colour, and their solutions are stable only when they contain large quantities of free alkali. If carbon dioxide is passed through them, or if they are diluted with much water, or made slightly acid, the liquid passes from a green to a blue and violet colour, the permanganate being formed, and the dioxide deposited:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

The manganates are also converted by direct oxidation into permanganates when they are dissolved in a large quantity of water containing dissolved oxygen.

Manganates are produced by the partial reduction of permanganates in alkaline solution, and this change occurs when small amounts of reducing agents such as alcohol and sodium thiosulphate are added to the red alkaline liquid. The latter also gradually turns blue and afterwards green simply on exposure to air, this being caused by the reducing action of the organic matter contained in the atmosphere. These reactions explain the changes of colour of the mineral chameleon. In alkaline solution the manganates act as powerful oxidising agents.

[1] *Ann. Phil.*, 1807, **16**, 130; 1808, **17**, 150.
[2] *Pogg. Ann.*, 1832, **25**, 287.
[3] Franke, *J. pr. Chem.*, 1887, [2], **6**, 893.
[4] *Journ. Chem. Soc.*, 1888, **53**, 175.

Potassium Manganate, K_2MnO_4, is formed when manganese dioxide is fused together with caustic potash. If the fusion takes place in the absence of air, the following reaction occurs:

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$

In the presence of air, or on the addition of nitre or potassium chlorate, a larger quantity of the product is obtained:

$$2KOH + MnO_2 + O = K_2MnO_4 + H_2O.$$

The deep-green coloured mass dissolves in a small quantity of water, forming a dark-green solution, from which, on evaporation in a vacuum, the salt separates out in small crystals isomorphous with those of potassium sulphate.

It may be prepared also by boiling a saturated solution of potassium permanganate with caustic potash solution of specific gravity 1·33 (Aschoff).

Sodium Manganate, Na_2MnO_4, is formed when a mixture of equal parts of manganese dioxide and caustic soda is heated for sixteen hours; the mass is then lixiviated with a small quantity of water and the solution cooled down, when the salt separates out in small crystals isomorphous with Glauber's salt, and having the composition $Na_2MnO_4,10H_2O$. These dissolve in water with partial decomposition, yielding a green solution. Sodium manganate is now used largely as a deodoriser.

Barium Manganate, $BaMnO_4$, is formed when manganese dioxide is heated with baryta or barium carbonate or nitrate, or when barium permanganate is heated with baryta water. It is an emerald-green powder, consisting of microscopic four-sided prisms or six-sided plates. It has a specific gravity of 4·85, and is insoluble in water, but is readily decomposed by acids. The employment of this salt in place of the poisonous Scheele's green has been suggested,[1] and it has been employed in a few instances, though not so generally as might be wished.

520 *Manganese Heptoxide*, Mn_2O_7, and *Permanganic Acid*, $HMnO_4$.—The first of these compounds, also termed permanganic anhydride, was noticed by Chevillot, and afterwards investigated by Thénard,[2] Aschoff,[3] and Terreil.[4] In order to

[1] Schad *Deutsch. Industriezeit.*, 1865, 118; Rosenstiehl, *Dingl. Polyt. Journ.*, 1865, **177**, 409.

[2] *Compt. rend.*, 1856, **42**, 389.

[3] *Pogg. Ann.*, 1860, **111**, 217.

[4] *Bull. Soc. chim.*, 1862, 40.

prepare this compound, pure potassium permanganate free from chlorine is gradually added to well-cooled highly concentrated sulphuric acid. The salt dissolves with an olive-green colour, and if the solution be cooled, and water carefully added, the heptoxide separates as a dark reddish-brown liquid[1] which does not solidify at $-20°$. It is extremely unstable, constantly evolving bubbles of oxygen on exposure to the air. These carry with them a small quantity of the heptoxide, and thus violet fumes are emitted. It rapidly absorbs moisture, and dissolves in water, yielding a deep violet-coloured solution, so much heat being thereby evolved that the liquid undergoes partial decomposition. It dissolves in concentrated sulphuric acid with an olive-green colour. On heating, it decomposes, with evolution of light and heat, and with violent explosion. The green solution contains the sulphate $(MnO_3)_2SO_4$:

$$2KMnO_4 + 2H_2SO_4 = (MnO_3)_2SO_4 + K_2SO_4 + 2H_2O,$$

and this on addition of water yields the heptoxide:

$$(MnO_3)_2SO_4 + H_2O = Mn_2O_7 + H_2SO_4.$$

Permanganic Acid, $HMnO_4$, is obtained in aqueous solution by adding the requisite quantity of dilute sulphuric acid to the barium salt or by electrolysing the potassium salt in a special form of apparatus and removing the alkali from the cathode compartment.[2] A deep red liquid is thus obtained, which exhibits a blue colour by reflected light, and possesses a bitter metallic taste. It decomposes on exposure to light or when heated gently, and still more rapidly when boiled, with evolution of oxygen and separation of the hydrated dioxide. It acts as a most powerful oxidising agent.

Permanganic acid is formed also when manganese nitrate or any manganous salt, with the exception of the halide compounds, is warmed with nitric acid and lead dioxide, with potassium bromate and dilute sulphuric acid,[3] with the higher oxides of bismuth and nitric acid,[4] or with ammonium persulphate, silver nitrate and nitric acid.[5]

A weak solution of permanganic acid continually evolves oxygen at a very slow rate, manganese dioxide being deposited,

[1] Franke, *J. pr. Chem.*, 1885, [2], **31**, 166.
[2] Morse and Olsen, *Amer. Chem. J.*, 1900, **23**, 431.
[3] Vitali, *Boll. Chim. Farm.*, 1898, **37**, 545.
[4] Schneider, *Dingl. Polyt. Journ.*, 1888, **269**, 224.
[5] Marshall, *Chem. News*, 1901, **83**, 76.

and the rate of decomposition is greatly increased by the presence of hydrated manganese dioxide.[1] When such a solution is shaken with hydrogen or carbonic oxide, the gas is rapidly absorbed and a considerable volume of oxygen evolved (Victor Meyer and Recklinghausen).[2] It has been suggested that this is due to the fact that the hydrated manganese dioxide simultaneously formed is at first present in a specially active condition and thus greatly increases the normal decomposition of the permanganic acid (Morse and Reese).

Permanganic acid has been obtained in the form of violet-black crystals, by evaporating the solution obtained by the action of barium permanganate and sulphuric acid. It decomposes very rapidly.[3]

Potassium Permanganate, $KMnO_4$, is prepared on the large scale by a process which will be described further on. For laboratory purposes it is best obtained according to the process given by Gregory. This consists in dissolving ten parts of caustic potash in the smallest quantity of water, then adding to this a mixture of seven parts of potassium chlorate and eight parts of manganese dioxide, evaporating the whole to dryness, and heating the residue until the potassium chlorate is completely decomposed. The dark-green mass is then lixiviated with boiling water, the solution allowed to deposit, and the liquid filtered through asbestos or gun-cotton. The clear solution deposits the crystals on standing. It is also formed when a solution of caustic potash is electrolysed with an anode consisting of ferro-manganese or manganese.[4]

Potassium permanganate is isomorphous with potassium perchlorate, with which it crystallises in all proportions. The crystals are almost black, and when freshly prepared possess a green metallic lustre, which, however, on exposure to the air becomes of a steel-blue tint without any further alteration in the salt taking place. The crystals have a specific gravity of 2·7, and yield a red powder. 100 parts of water dissolve[5] 5·31 parts of the salt at 15°, 25·03 parts at 100°, forming a deep

[1] Morse, Hopkins and Walker, *Amer. Chem. J.*, 1896, **18**, 401; Morse, *Ber.*, 1897, **30**, 48; Morse and Reese, *Amer. Chem. J.*, 1898, **20**, 521; Morse and Byers, *ibid.*, 1900, **23**, 313; Olsen, *ibid.*, 1903, **29**, 242.

[2] *Ber.*, 1896, **29**, 2549; Hirtz and Meyer, *ibid.*, 2828.

[3] Muir, *Journ. Chem. Soc.*, 1907, **91**, 1485.

[4] White, *J. Physical Chem.*, 1906, **10**, 502.

[5] Baxter, Boylston, and Hubbard, *J. Amer. Chem. Soc.*, 1906, **28**, 1336; Patterson, *ibid.*, 1734.

purple-coloured solution. On heating to 240° they decompose as follows:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

Jones[1] has shown that hydrogen and phosphine decompose potassium permanganate, and that oxygen is evolved together with carbon dioxide when sulphuric acid acts on permanganate in presence of oxalic acid.

Mixed with sulphur or phosphorus, a material is obtained which takes fire or explodes violently on percussion, and a mixture of the salt with charcoal burns like tinder.

Potassium permanganate is largely used as an oxidising agent, both in analytical work and for the preparation of many organic oxidation products. In alkaline solution it is first converted into manganate, which afterwards loses a further amount of oxygen and yields the hydrated dioxide, three atoms of the oxygen contained in two molecules of the salt being employed in the oxidation:

$$(1)\ 2KMnO_4 + 2KHO = 2K_2MnO_4 + H_2O + O,$$
$$(2)\ 2K_2MnO_4 + 2H_2O = 2MnO_2 + 4KHO + 2O.$$

It is in this way, for example, that potassium permanganate acts when it is brought into contact with a hot solution of a manganous salt, the whole of the manganese being precipitated as dioxide (Volhard); three-fifths of this is therefore formed by the oxidation of the manganese salt added and the remaining two-fifths by the reduction of the permanganate:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

In acid solution the manganese of the permanganate is finally converted into a salt corresponding to the monoxide, MnO, five atoms of oxygen being rendered available:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Thus the action of acid potassium permanganate solution on ferrous sulphate, in presence of sulphuric acid, is represented as follows:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

[1] *Journ. Chem. Soc.*, 1878, **33**, 95.

The acid solution of potassium permanganate is reduced by hydrogen peroxide with evolution of oxygen,[1] half of which is due to the reduction of the peroxide, half to that of the permanganate:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

Sodium Permanganate, $NaMnO_4$, is obtained in a similar way to the potassium salt, and is distinguished from it by being deliquescent, and therefore crystallising with difficulty.

Ammonium Permanganate, NH_4MnO_4, is obtained by the decomposition of the potassium salt with ammonium chloride. It is isomorphous with potassium permanganate, and decomposes readily when gently heated,[2] forming ammonium nitrate, oxides of nitrogen, and an oxide of manganese of the composition $22MnO_2,MnO$. It explodes when rapidly heated, or when subjected to percussion.

Barium Permanganate, $Ba(MnO_4)_2$, forms hard, almost black prisms, soluble in water. It is obtained by passing a current of carbon dioxide through water containing barium manganate in suspension,[3] or by the action of barium chloride on silver permanganate.

Silver Permanganate, $AgMnO_4$, separates out in large regular crystals when warm solutions of silver nitrate and potassium permanganate are mixed. It dissolves in 190 parts of water at 15°, and is much more soluble in warm water. The solution decomposes on boiling.

Condy's Disinfecting Liquid.—Potassium permanganate has been employed for a long time in the laboratory as a powerful oxidising agent, and is largely used in volumetric analysis. Hofmann was the first, in the year 1859, to show that this salt together with the other manganates and permanganates acts as a valuable disinfecting agent,[4] and its application for this purpose has become now so general that these compounds, which at that time were only found in the laboratory, are now made in thousands of tons. Owing to the ease with which it is reduced by organic matter, the permanganate should always be added to the material to be disinfected in such quantity that a permanent green or red coloration remains. For disinfecting

[1] On the nature of this reaction see Baeyer and Villiger, *Ber.*, 1900, **33**, 2488, where the literature is quoted; Bach, *Ber.*, 1901, **34**, 3851.

[2] Christensen, *Zeit. anorg. Chem.*, 1900, **24**, 203.

[3] Böttger, *J. pr. Chem.*, 1863, **90**, 156.

[4] See Kronig and Paul, *Zeit. Hygiene*, 1897, **35**, 73.

purposes it is not necessary to employ the pure, well-crystallised salt which is used in the laboratory, so a commercial article consisting of a mixture, more or less pure, of manganate and permanganate of sodium is used. This substance is obtained by mixing the caustic soda obtained from 1,500 kilos. of soda-ash with 350 kilos. of finely divided manganese dioxide in a flat vessel, and heating this mixture for forty-eight hours to dull redness. The product, containing about 26 per cent. of pure manganate, is either used in that form, or lixiviated with water, and the solution either boiled down to the requisite degree of strength or evaporated to dryness. If the manganate is to be completely converted into permanganate it is neutralised with sulphuric acid, and the solution concentrated until Glauber's salt separates out; these crystals are then removed and the liquid further evaporated.[1]

Manganese and the Halogens.

521 *Manganous Fluoride*, MnF_2, is obtained by dissolving metallic manganese or the carbonate in hydrofluoric acid, the compound being deposited as a white crystalline powder when the solution is boiled. It is formed also as a rose-coloured mass by the action of gaseous hydrogen fluoride on manganese. It is insoluble in water but may be recrystallised from fused manganese chloride and then forms rose-coloured prisms of sp. gr. 3·98, melting at 856°. It dissolves in strong acids, yields an oxyfluoride when boiled with water, and is completely reduced by hydrogen at 1000°.[2]

Manganic Fluoride, MnF_3, is obtained by the action of fluorine on manganous iodide in purple pseudomorphs of sp. gr. 3·54. It decomposes, when heated, into manganous fluoride and fluorine, dissolves in strong acids, forming unstable dark brown solutions, and is decomposed by water.[3] A hydrated trifluoride, $MnF_3,3H_2O$, is obtained in ruby-red crystals by dissolving the sesqui- or the di-oxide in hydrofluoric acid, and readily forms compounds with the alkali fluorides.[4]

Potassium Manganifluoride, K_2MnF_6, is obtained by decomposing potassium manganate with water and dissolving the

[1] Hofmann, *Report Exhib.*, 1862, 109.
[2] Moissan and Venturi, *Compt. rend.*, 1900, **130**, 1158.
[3] Moissan, *Compt. rend.*, 1900, **130**, 622.
[4] Christensen, *J. pr. Chem.*, 1887, [2], **35**, 57, 161, 541.

resulting potassium manganite in a mixture of hydrofluoric acid and potassium fluoride. It forms small golden yellow hexagonal tablets and is decomposed by water, but may be recrystallised from hydrofluoric acid. It yields a dark brown-coloured solution in hydrochloric acid which evolves chlorine when gently heated. A *rubidium salt* of similar properties has also been obtained.[1]

Manganous Chloride, $MnCl_2$, is formed when the metal is burned in chlorine gas, or when hydrogen chloride is passed over heated manganous carbonate. Prepared in this way manganese chloride is a pale rose-coloured mass, having a lamino-crystalline structure. When heated to redness it fuses to an oily liquid, and decomposes in moist air at this temperature with formation of hydrochloric acid and the oxides of manganese. Manganous chloride is obtained in solution by dissolving the carbonate or any of the oxides in hydrochloric acid. For this purpose the residues from the preparation of chlorine by means of pyrolusite and hydrochloric acid may be utilised. These are always coloured yellow, from the presence of ferric chloride, and contain an excess of acid. They must be evaporated to drive off the acid, then diluted with water, and a tenth of the solution precipitated with sodium carbonate. The precipitate, consisting of manganese carbonate and ferric hydroxide, is then well washed with hot water and boiled with the remainder of the liquid. By this means the whole of the iron is precipitated as ferric oxide, and in order to ascertain that the precipitation of the iron is complete, a small portion of the liquid is filtered off and a drop or two of ferrocyanide of potassium added; if free from iron only a white precipitate will be formed; if, however, the precipitate has a bluish colour, iron is still contained in solution, and the liquid requires to be boiled for a long time with manganese carbonate. The filtrate may contain copper, barium, and calcium. The first of these metals is removed by passing a current of sulphuretted hydrogen through the liquid. If the last two metals are present the manganese is best precipitated by ammonium sulphide, the precipitate well washed with hot water, and then dissolved in hydrochloric acid. On evaporation, the concentrated solution deposits between 15° and 20° light pink-coloured monoclinic crystals of the hydrated chloride $MnCl_2,4H_2O$. This hydrate is transformed at 57·85° into the hydrate $MnCl_2,2H_2O$, which is

[1] Weinland and Lauenstein, *Zeit. anorg. Chem.*, 1899, **20**, 40.

stable up to 198° and then passes into the anhydrous salt. Below −2° the hydrate $MnCl_2,6H_2O$ is formed.[1] In addition to these an isomeric β-tetrahydrate is known (Marignac)[2] which also forms monoclinic crystals, but of a different form from the ordinary tetrahydrate, being isomorphous with those of hydrated ferrous chloride, $FeCl_2,4H_2O$. The dihydrate may be prepared by heating the tetrahydrate for some time at 60° or passing hydrogen chloride into an alcoholic solution of the chloride. One hundred parts of water dissolve :

At	8°	25°	30°	57·85°	80°	100°
$MnCl_2$	6·2	77·2	80·7	105·7	112·7	116.

This salt is also soluble in alcohol, forming a green solution which burns on ignition with a red flame. Manganese chloride forms double salts with the chlorides of the alkali metals and with some other chlorides.

Manganese Trichloride, $MnCl_3$, and *Manganese Tetrachloride*, $MnCl_4$, have only recently been obtained in the solid state. When either of the oxides, Mn_3O_4, Mn_2O_3, or MnO_2, is added to cold concentrated hydrochloric acid, a dark brown solution is formed, chlorine being simultaneously produced when the dioxide is employed. This solution appears to contain the trichloride,[3] and yields double salts of the type $MnCl_3,2RCl$, with the chlorides of potassium and ammonium.[4] The addition of water to the solution precipitates a mixture of hydrated oxides (Pickering).[5] When the dark brown solution is heated, chlorine is evolved and manganous chloride remains :

$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

When manganese dioxide is treated with ether saturated with hydrochloric acid, a deep green solution is obtained, which was considered by Nicklés[6] to contain the tetrachloride, $MnCl_4$, and by Franke[7] to contain the compound $MnCl_2,MnCl_4$.

[1] Kuznetzóff, *J. Russ. Phys. Chem.* Soc., 1898, **30**, 741 ; Dawson and Williams, *Zeit. physikal. Chem.*, 1899, **31**, 59. See also Richards and Briggs, *ibid.*, 1898, **28**, 313.

[2] *Compt. rend.*, 1857, **45**, 650.

[3] Pickering, *Journ. Chem. Soc.*, 1879, **35**, 654.

[4] Neumann, *Monatsh.*, 1894, **15**, 489 ; Rice, *Journ. Chem. Soc.*, 1898, **73**, 258.

[5] See also Fisher, *Journ. Chem. Soc.*, 1878, **33**, 409 ; Christensen, *J. pr. Chem.*, 1887, [2], **35**, 57, 161, 541.

[6] *Ann. Chim. Phys.*, 1865, [4]. **5**, 169 ; 1867, [4], **10**, 318.

[7] *J. pr. Chem.*, 1888, [2], **36**, 31, 453.

It is, however, probable that this green liquid contains the trichloride and not the tetrachloride, since it yields double salts with the hydrochlorides of pyridine and quinoline of the type $MnCl_3,2RHCl$, and almost the whole of the manganese in the solution can be precipitated in this form. Similar but more concentrated green solutions can be prepared by the action of alcoholic hydrochloric acid on manganese dioxide or potassium permanganate.[1]

When dry hydrogen chloride is passed into carbon tetrachloride in which manganese dioxide is suspended, a solid product is obtained which consists of manganese trichloride and tetrachloride. On treating this with anhydrous ether, the trichloride dissolves, forming a deep violet-coloured solution. A reddish-brown residue of the tetrachloride remains. The trichloride is a black solid, having a greenish tinge, which is decomposed by water. The tetrachloride is reddish-brown and is stable at ordinary temperatures, but is decomposed by moisture.[2]

Derivatives of the tetrachloride can be obtained by boiling potassium permanganate with glacial acetic acid, and saturating the resulting reddish-brown solution with hydrochloric acid. A dark crystalline precipitate of *potassium manganichloride*, $MnCl_4,2KCl$, is thus produced, which rapidly loses chlorine in moist air, but may be preserved in dry air for some time. If potassium acetate be added to the liquid before it is saturated with hydrochloric acid, Neumann's salt, $MnCl_3,2KCl$, is obtained (Meyer and Best).

Permanganic Oxychloride, MnO_3Cl.—This chloride of permanganic acid was first prepared by Dumas:[3] he did not, however, analyse the compound, but from its mode of decomposition considered it to be manganese heptachloride, $MnCl_7$. It is obtained by gradually adding fused sodium chloride to a solution of potassium permanganate in concentrated sulphuric acid. A yellow gas is then evolved, which when passed through a freezing mixture condenses to a greenish-brown liquid. This when exposed to the air emits a purple-red vapour, which possesses the peculiar smell of the oxides of chlorine, and like them acts most violently upon the mucous membrane, so that the smallest quantity of the chloride contained in commercial permangan-

[1] Meyer and Best, *Zeit. anorg. Chem.*, 1900, **22**, 169.
[2] Holmes, *J. Amer. Chem. Soc.*, 1907, **29**, 1277.
[3] *Ann. Chim. Phys.*, 1827, [2], **36**, 81.

ate can be thus readily detected.[1] When heated it explodes violently, and water decomposes it with formation of permanganic acid and hydrochloric acid. These substances, however, mutually decompose with formation of free chlorine and manganese dioxide. A corresponding oxyfluoride, MnO_3F, exists, and was first prepared by Wöhler.[2]

Manganous Bromide, $MnBr_2$, is obtained by heating the powdered metal in bromine vapour, and when the compound is fused, it is obtained as a pale-red mass. When the carbonate is dissolved in hydrobromic acid the hydrated bromide, $MnBr_2,4H_2O$, is obtained, and this was found by Marignac to be isomorphous with the ordinary form of the chloride.

Manganous Iodide, $MnI_2,4H_2O$, is obtained crystallised in colourless deliquescent needles, which become coloured on exposure to air. Hydrates with $5H_2O$ and $9H_2O$ are formed below $-2{\cdot}7°$ and $-9{\cdot}3°$ respectively.[3]

Manganese Tetriodate, $Mn(IO_3)_4$, is not known in the free state, but a double salt with potassium iodate, $Mn(IO_3)_4,2KIO_3$, is formed as a brownish-violet, insoluble, crystalline powder when hydrated manganese dioxide is boiled with iodic acid and potassium iodate.[4]

Manganese and Sulphur.

522 *Manganese Monosulphide*, MnS, occurs as the mineral manganese blende, or alabandite, forming a steel-grey crystalline mass with a green streak, and sometimes observed in cubes and octahedra. It has a specific gravity of 4·04, and occurs in veins in the coal mines in Transylvania, and in Freiberg and Mexico. It may be obtained artificially in the form of a dark grey powder, which melts at a high temperature forming a steel-grey crystalline mass, by heating the monoxide, the carbonate, or the sulphate in a current of hydrogen sulphide (Arfvedson), or in green octahedra by heating manganous sulphide with a little sulphur in the electric furnace.[5] Ammonium sulphide and the other monosulphides of the alkali metals precipitate anhydrous manganese sulphide from a solution of a manganous salt in the form of a light flesh-coloured precipitate,

[1] Aschoff, *Pogg. Ann.*, 1860, **111**, 217. [2] *Pogg. Ann.*, 1827, **9**, 619.
[3] Kuznetzoff, *J. Russ. Phys. Chem. Soc.*, 1900, **32**, 290.
[4] Berg, *Compt. rend.*, 1899, **128**, 673.
[5] Mourlot, *Compt. rend.*, 1895, **121**, 202.

which dissolves readily in dilute acids and oxidises on exposure to the air, assuming a brown tint. When left in contact with ammonium sulphide, or heated to 300°,[1] and when suspended in a dilute solution of sulphuretted hydrogen and exposed to a low temperature, it passes into the green crystalline sulphide.[2] According to Olsen and Rapalje a grey form of the sulphide also exists and the sulphide precipitated by ammonium sulphide is a mixture of this and a red form. The sulphide precipitated by sodium sulphide does not contain the grey form,[3] and does not become green when left in contact with excess of the precipitant.

Manganese sulphide combines with the sulphides of the alkali metals to form salts.[4] The potassium salt, $K_2S,3MnS$, is formed as a dark-red crystalline mass when anhydrous manganese sulphate is gradually heated to redness with three parts of potassium carbonate, 0·2 part of lamp-black, and excess of sulphur.

Manganese Disulphide, MnS_2.—This substance is found as the mineral hauerite in crystals belonging to the regular system. They possess a metallic adamantine lustre, and a reddish-brown colour, and occur in clay at Kalinka in Hungary, together with sulphur and gypsum.

Manganous Sulphate, $MnSO_4$, is best prepared by mixing commercial black oxide of manganese to a paste with sulphuric acid and heating the mixture in a crucible to strong redness, when the greater part of the iron sulphate is destroyed. The filtrate obtained after lixiviating the residue is then heated with a small quantity of manganous carbonate in order to precipitate the last traces of iron.

It has a specific gravity of 3·1, and is decomposed at a bright red heat, leaving a residue of red oxide of manganese. Manganous sulphate forms a number of hydrates and the equilibrium curve for this substance and water is one of great complexity. Below 8° the heptahydrate separates out, between 8° and 27° the pentahydrate is the stable form, and above 27° the monohydrate. The solubility of the latter decreases as the temperature rises, so that a maximum of solubility exists at 27°. In addition to these stable forms, several labile hydrates exist, the

[1] Antony and Donnini, *Gazz.*, 1893, **23**, i., 560.

[2] Villiers, *Compt. rend.*, 1895, **120**, 322.

[3] *J. Amer. Chem. Soc.*, 1904, **26**, 1615, where the literature is quoted.

[4] Völker, *Annalen*, 1846, **59**, 35; Brunner, *Arch. sci. phys. nat.*, 1889, **22**, 68.

most important of these being the tetrahydrate, which separates at about 30° in rose-coloured prisms of sp. gr. 2·097 (Kopp). Several other hydrates have been described, but it is doubtful whether they all exist.[1] 100 parts of water dissolve:

At	0°	9°	15°	27°	50°	70°	100°
$MnSO_4$	53·2	59·3	61·1	66	59·5	52	33·2.

The last trace of water is expelled from the monohydrate only at 450°.

Manganous sulphate is insoluble in absolute alcohol, this liquid removing a portion of the water from the hydrates. Finely crystalline double sulphates[2] are formed when manganous sulphate and the sulphates of the alkali metals are crystallised together; these belong to the isomorphous series $R^{I}_2SO_4$, $R^{II}SO_4,6H_2O$.

Manganous Aluminium Sulphate, $MnSO_4,Al_2(SO_4)_3,24H_2O$.—This substance occurs as the mineral apjohnite found in Algoa Bay in South Africa.[3]

Manganic Sulphate, $Mn_2(SO_4)_3$.—Manganic oxide and hydroxide dissolve with difficulty in sulphuric acid. The red oxide, Mn_3O_4, on the other hand, dissolves readily, yielding a purple-red solution. If the finely divided precipitated dioxide is treated with sulphuric acid, oxygen is evolved, and at a temperature of 138° a green liquid is obtained from which the sulphate is precipitated as a non-crystalline powder. In order to purify this salt it is brought on to a porous porcelain plate, when the greater part of the sulphuric acid is absorbed; the residue is then washed with pure nitric acid and the salt is allowed to dry in absence of air on another porous plate, and then heated to 150°.[4]

Manganese Alums.—Manganese forms a series of alums, $R^{I}_2SO_4,Mn_2(SO_4)_3,24H_2O$, which crystallise in pink or red octahedral forms. They are decomposed by water, but are stable in a solution of 1 volume of sulphuric acid diluted with 3 of water, provided that the temperature is kept low. The potassium and ammonium salts are extremely unstable and have not been obtained pure, but the cæsium and rubidium salts

[1] Schieber, *Monatsh.*, 1898, **19**, 280; Cottrell, *J. Physical Chem.*, 1900, **4**, 637; Richards and Fraprie, *Amer. Chem. J.*, 1901, **26**, 75; compare Linebarger, *ibid.*, 1893, **15**, 225.

[2] See also Scott, *Journ. Chem. Soc.*, 1897, **71**, 587; Mallet, *ibid.*, 1900, **77**, 221; 1902, **81**, 1549.

[3] *Phil. Mag.*, 1856, [3], **12**, 103. [4] Carius, *Annalen*, 1856, **98**, 53.

can be prepared. The salts obtained by the addition of the sulphates of potassium and ammonium to manganic sulphate and evaporating are not true alums, but contain less water of crystallisation.[1] An anhydrous ammonium manganic sulphate has also been obtained and forms violet crystals which are decomposed by water.[2]

Manganic Cæsium Alum, $Cs_2SO_4,Mn_2(SO_4)_3,24H_2O$, may be prepared by dissolving cæsium sulphate and manganic acetate, $Mn_2(C_2H_3O_2)_3$ (obtained by the action of potassium permanganate on manganous acetate dissolved in glacial acetic acid), in dilute sulphuric acid and cooling to $-20°$ (Christensen). It can be obtained also by electrolysing at 10–15° a solution of manganous sulphate and cæsium sulphate in dilute sulphuric acid placed in the anode compartment of an electrolytic cell.[3] It forms coral-red crystals of the regular system (class 30, p. 201) and is decomposed by water. It melts at 40° in its water of crystallisation.

The *Rubidium Alum* closely resembles the cæsium salt but decomposes at about 15°, whilst the potassium and ammonium alums decompose at still lower temperatures (Christensen).

Manganous Dithionate, $MnS_2O_6,3H_2O$.—This salt is of interest inasmuch as it is employed for the preparation of dithionic acid (Vol. I., 457). It is obtained by passing sulphur dioxide through water in which finely divided manganese dioxide is suspended. The solution always contains a small quantity of manganous sulphate, and for this reason baryta water is added as long as a precipitate of barium sulphate is formed. Manganous dithionate is deposited in easily soluble rhombohedral crystals.

Manganese and the Elements of the Nitrogen Group.

523 *Manganese Nitride.*—The compound Mn_5N_3 is produced when nitrogen is passed over finely divided manganese at a red heat. When ammonia is substituted for nitrogen, the substance formed has the composition Mn_3N_2. Both of these form dark-coloured powders which yield ammonia when they are heated in hydrogen or fused with potash.[4]

[1] Christensen, *Zeit. anorg. Chem.*, 1901, **27**, 328.
[2] Lepierre, *Compt. rend.*, 1895, **120**, 924.
[3] Piccini, *Zeit. anorg. Chem.*, 1898, **17**, 355; 1899, **20**, 12.
[4] Prelinger, *Monatsh.*, 1894, **15**, 391.

Manganous Nitrate, $Mn(NO_3)_2$.—The hydrate with $6H_2O$ crystallises with difficulty in colourless deliquescent needles which melt at 25·8°, and are readily soluble in alcohol. A hydrate with $3H_2O$ also exists[1] which is stable above 25° and melts at 35·5°. The nitrate decomposes at 129·5, at which temperature a black deposit of manganese oxides is formed.

Phosphides of Manganese.—The phosphide Mn_3P_2 was obtained by Wedekind and Veit[2] by heating manganese with red phosphorus in an atmosphere of hydrogen, and forms lustrous needles of sp. gr. 5·12, which are magnetic and dissolve in warm nitric acid. A compound of this formula, but insoluble in nitric acid, was prepared by Granger[3] by passing phosphorus vapour and hydrogen over manganous chloride, whereas Wedekind and Veit obtained a magnetic compound Mn_5P_2 in this way.

Manganous Phosphates.—These salts have been investigated by Heintz,[4] Debray,[5] Bödecker,[6] and Erlenmeyer.[7] The normal manganous orthophosphate, $Mn_3(PO_4)_2,7H_2O$, is a white imperfectly crystalline precipitate. The *monohydrogen salt*, $HMnPO_4,3H_2O$, forms small prismatic rose-coloured rhombic crystals slightly soluble in water, and the *dihydrogen phosphate*, $H_4Mn(PO_4)_2,2H_2O$, crystallises in red four-sided prisms which deliquesce on exposure to the air, decomposing into free phosphoric acid and the preceding salt.[8]

Manganous salts are precipitated by ammonium phosphate as *manganous ammonium phosphate*,[9] $Mn(NH_4)PO_4,H_2O$, which is converted by ignition into the *pyrophosphate*, $Mn_2P_2O_7$.

Manganic Phosphates.—Both manganic oxide and the dioxide dissolve in a concentrated solution of phosphoric acid, in the latter case with evolution of oxygen, with formation of a deep violet liquid, from which a violet-coloured crystalline mass separates out (Gmelin). This decomposes in contact with water, and manganic hydroxide is precipitated from the solution by alkalis. On evaporating the red solution a peach-blossom-coloured powder separates, consisting of manganic metaphosphate, $Mn(PO_3)_3,H_2O$.[10] The normal phosphate

[1] Funk, *Ber.*, 1899, **32**, 96.
[2] *Ber.*, 1907, **40**, 1268.
[3] *Compt. rend.*, 1897, **124**, 190.
[4] *Pogg. Ann.*, 1848, **74**, 450.
[5] *Annalen*, 1849, **69**, 208.
[6] *Ann. Chim. Phys.*, 1861, [3], **61**, 433.
[7] *Annalen*, 1877, **190**, 191.
[8] See also Viard, *Compt. rend.*, 1899, **129**, 412.
[9] Dakin, *Zeit. anal. Chem.*, 1900, **39**, 784.
[10] Hermann, *Pogg. Ann.*, 1848, **74**, 303. See also Barbier, *Compt. rend.* 1902, **135**, 1054, 1109.

$MnPO_4,H_2O$, an acid pyrophosphate, $MnHP_2O_7$, and the salts $MnKP_2O_7$ and $Mn_4P_6O_{21},14H_2O$,[1] have also been prepared.[2]

Manganese Arsenides.—Two arsenides of manganese are known,[3] the first of which, MnAs, is non-magnetic, but is converted by heating into the magnetic compound, Mn_2As.

Manganous Arsenate.—When arsenic acid is saturated with manganese carbonate, a sparingly soluble salt having the composition $HMnAsO_4$ is formed. This dissolves readily in arsenic acid with formation of the salt $H_4Mn(AsO_4)_2$, which latter crystallises in rectangular plates.

Several double salts with the alkali arsenates are also known.[4]

Manganese Antimonide, MnSb, can be prepared by the direct union of the elements, or by igniting a mixture of antimony with manganese thermite, and may be purified by treatment with bromine. It forms a black crystalline powder of specific gravity 5·6, and is strongly magnetic.[5]

Manganese and Boron.

524 *Manganese Diboride,* MnB_2, is produced when a mixture of manganese thermite and boron is ignited or the oxides reduced with boron, and may be purified by treatment with chlorine. It forms grey-black crystals, which, when pure, are non-magnetic, decompose in warm water, and dissolve in concentrated acids.[6]

Manganese Monoboride, MnB, is prepared by the reduction of red oxide of manganese with boron at a white heat in a magnesia crucible, or by the direct union of its elements, and forms a black crystalline powder of specific gravity 6·2, which resembles the diboride in its properties but is strongly magnetic and dissolves more readily in acids.[7]

Manganese Borate, $MnH_4(BO_3)_2$, is formed as an almost

[1] Auger, *Compt. rend.*, 1901, **133**, 94.

[2] Christensen, *J. pr. Chem.*, 1883, [2], **28**, 1; Schjerning, *J. pr. Chem.*, 1892, [2], **45**, 515.

[3] Wedekind, *Zeit. Elektrochem.*, 1905, **11**, 850; *Ber. deutsch. physik. Ges.*, 1906, **4**, 412.

[4] Lefèvre, *Compt. rend.*, 1890, **110**, 405.

[5] Wedekind and Fetzer, *Ber.*, 1907, **40**, 1266.

[6] Wedekind, *Ber.*, 1905, **38**, 1228; Wedekind and Fetzer, *Ber.*, 1907, **40**, 1264; Binet du Jassoneix, *Ber*, 1907, **40**, 3193.

[7] Binet du Jassonneix, *Compt. rend.*, 1904, **139**, 1209; 1906, **142**, 1336.

white powder when manganese sulphate is added to a solution of borax, and the precipitate is dried at 100°. When it is heated to redness it yields the metaborate, $Mn(BO_2)_2$. The precipitated salt is used in the preparation of drying oils and oil varnishes,[1] the commercial salt being a mixture of varying composition.[2]

Manganese and the Elements of the Carbon Group.

525 *Manganese Carbide*, Mn_3C, is formed when red oxide of manganese is heated with charcoal or calcium carbide in the electric furnace. It has the specific gravity 6·89, and when treated with water yields equal volumes of hydrogen and methane:

$$Mn_3C + 6H_2O = CH_4 + H_2 + 3Mn(OH)_2.$$

It burns readily in oxygen, and is easily attacked by fluorine and chlorine.[3] When very strongly heated it dissociates, the manganese volatilises, and the carbon remains as graphite.[4]

Manganese Carbonate, $MnCO_3$, forms an isomorphous constituent of chalybite and dolomite, and occurs also in the pure state in the rose-red crystals of manganese spar, rhodochrosite or dialogite. All these minerals crystallise, like calc-spar, in rhombohedra, but manganocalcite, $(Mn,Ca,Mg)CO_3$, is isomorphous with aragonite.

Hydrated manganese carbonate is obtained as a white precipitate by mixing a solution of the chloride or sulphate of manganese with sodium carbonate. In the moist state it soon becomes brown-coloured on exposure to the air; it dissolves in 8,000 parts of pure water, and in about half the quantity of water saturated with carbon dioxide.

Manganese and Cyanogen.—When a concentrated solution of manganese acetate is warmed with solid potassium cyanide a green precipitate is thrown down of $KCN,Mn(CN)_2$; this gradually disappears, and in its place dark blue crystals of *potassium manganocyanide*, $K_4Mn(CN)_6,3H_2O$, are formed.[5] The manganocyanide is obtained also when manganous carbonate is heated to a temperature of from 40° to 50° with a

[1] Hartley and Ramage, *Journ. Chem. Soc.*, 1893, **63**, 129.
[2] See Endemann and Paisley, *Zeit. angew. Chem*, 1903, **16**, 175.
[3] Moissan, *Compt. rend.*, 1896, **122**, 421; 1897, **125**, 839.
[4] Gin and Leleux, *Compt. rend.*, 1898, **126**, 749.
[5] Eaton and Fittig, *Annalen*, 1868, **145**, 157.

solution of potassium cyanide.[1] The salt crystallises in deep violet-blue efflorescent tetragonal tablets. Its solution oxidises on exposure to air with formation of *potassium manganicyanide*, $K_3Mn(CN)_6$, which crystallises in dark-red prisms. This latter salt when brought into contact with potassium amalgam in aqueous solution is again transformed into manganocyanide. The constitution of these complex salts will be referred to under the corresponding iron compounds.

Manganese Thiocyanate, $Mn(SCN)_2$, may be prepared from manganous sulphate and barium thiocyanate. The anhydrous salt is yellow, and forms a green hydrate with $3H_2O$, which crystallises at the ordinary temperature. Concentrated aqueous solutions are green, but become pink when they are diluted (Kumakoff).[2]

Silicides of Manganese.—Some doubt exists as to the number of definite compounds formed by these elements. A study of the freezing point curve for mixtures of the two[3] indicates the existence of the two compounds, Mn_2Si and MnSi, whilst in addition to these the compounds $MnSi_2$[4] and Mn_3Si_2[5] have been described.

The silicide, Mn_2Si, is formed when the two elements are heated together in the electric furnace,[6] by firing a mixture of silica, manganese oxide, and aluminium, or by heating a mixture of potassium silicofluoride, red oxide of manganese, copper, and sodium (Lebeau). It is a very hard brittle mass, which has a metallic lustre and steel-grey colour and a specific gravity of 6·4. It is not decomposed by water at the ordinary temperature, but it is attacked by steam, oxygen, and chlorine at a red heat, and dissolves in hydrochloric acid. Fluorine decomposes it at the ordinary temperature.

The *monosilicide*, MnSi, forms hard lustrous tetrahedral crystals of specific gravity 5·9, whilst the *disilicide*, $MnSi_2$, forms dark-grey octahedral crystals of specific gravity 5·24. The compound described by Gin of the formula Mn_3Si_2 is probably impure Mn_2Si (Lebeau).[7]

[1] Descamps, *Ann. Chim. Phys.*, 1881, [5], **24**, 178.
[2] Quoted by Grossmann, *Ber.*, 1905, **37**, 559.
[3] Doerinckel, *Zeit. anorg. Chem.*, 1906, **50**, 117.
[4] de Chalmot, *Amer. Chem. J.*, 1896, **18**, 536.
[5] Gin, *Compt. rend.*, 1906, **143**, 1229.
[6] Vigouroux, *Compt. rend.*, 1895, **121**, 771; 1905, **141**, 722; Lebeau, *Compt. rend.*, 1903, **136**, 89, 231; *Bull. Soc. chim.*, 1903, [3], **29**, 797; *Ann. Chim. Phys.*, 1904, [8], **1**, 553.
[7] *Compt. rend.*, 1907, **144**, 85.

Manganous Silicates occur as isomorphous constituents of many minerals, and some naturally occurring manganese silicates are also known. Thus, for instance, rhodonite, $MnSiO_3$, occurs in light brownish-red transparent triclinic crystals, and tephroite, Mn_2SiO_4, crystallises in the tetragonal system in rose-red, brown, or grey masses, and usually occurs together with rhodonite.

Detection and Estimation of Manganese.

526 Manganese is distinguished by forming a flesh-coloured sulphide readily soluble in dilute acids. In the course of analysis manganese is thrown down with the sulphides and hydroxides of the metals which are precipitated by ammonium sulphide. If the precipitate be treated with very dilute cold hydrochloric acid, the sulphides of cobalt and nickel, if present, remain undissolved. The solution is heated in order to remove the sulphuretted hydrogen, oxidised with potassium chlorate, and an excess of caustic soda is added. Iron, manganese, and uranium are thus thrown down as hydroxides. The washed precipitate is then dissolved in hydrochloric acid, the liquid neutralised, and ammonia and ammonium chloride added, when the whole of the metals, with the exception of manganese, are thrown down; the filtrate is then evaporated to dryness, and the residues heated to get rid of ammonium salts. The mass which remains can be treated in various ways for the detection of manganese. The simplest plan is to fuse a small quantity of the residue with caustic soda and saltpetre, when the dark-green potassium manganate is formed, and this colour becomes deep blue on cooling. It dissolves in water with a green colour, which on addition of a little nitric acid turns red. Other characteristic reactions for the manganese salts are the following. Potash and soda precipitate the white hydroxide, which soon becomes brown on exposure to air. Ammonia in the presence of ammonium chloride produces no immediate precipitate, but the solution rapidly absorbs oxygen from the air, brown manganic hydroxide being deposited. When a manganese compound is fused with borax an amethyst-coloured bead is obtained in the outer flame, and this in the inner flame becomes colourless.

The non-luminous gas flame is coloured green by manganese chloride, and this exhibits a spectrum in which the lines in the green and yellow are:[1] 5587(α), 5392(β), and 5195(γ).

[1] Hoppe-Seyler, *J. Chem.*, 1870, **110**, 303.

The spark spectrum of manganese contains a large number of bright lines, of which the most important are: 6022, 6017, and 6014 in the orange; 4824 and 4784 in the green; 4766, 4762, and 4754 in the blue; 4235 and 4228 in the indigo (Lecoq de Boisbaudran).

The absorption spectrum of permanganic acid and its potassium salt exhibits in very dilute solution five distinct bands; a more concentrated solution gives continuous absorption in the yellow and green; and this is observed also in certain solutions of manganic salts. The latter, however, do not show the bands on dilution. The manganous salts also show a characteristic absorption spectrum, chiefly in the ultra-violet.[1]

In order to estimate manganese gravimetrically it may be precipitated as the carbonate, sulphide, or phosphate. Frequently, however, it is thrown down as the peroxide by treating the solution with bromine water and ammonia, or nitric acid and a chlorate. This is then converted by ignition into the red oxide, Mn_3O_4, in which condition the manganese is weighed. The sulphide on heating in the air is also converted into the same oxide. This oxide is, however, very liable to reduction or oxidation, and the amount of available oxygen in it should always be ascertained volumetrically. It can also be estimated electrolytically.

Manganese always occurs in nature together with iron. In order to separate these the solution is heated with ammonium chloride, neutralised with the requisite quantity of ammonia, and the iron precipitated with ammonium acetate. The manganese can then be estimated in the filtrate in the above way.

Manganese may be estimated volumetrically by titration with potassium permanganate in presence of zinc sulphate (p. 1143), or by conversion into permanganate, which is then estimated by titration with standard oxalic acid, hydrogen peroxide, or some other reducing agent. When small quantities are concerned this is best done by boiling the manganese salt with concentrated nitric acid, solid lead peroxide, and a little dilute sulphuric acid, and filtering the resulting liquid through asbestos, or by digesting the salt with nitric acid and sodium bismuthate, or a persulphate, sulphuric acid and silver nitrate.

Manganese may also be precipitated as the hydrated dioxide by boiling with dilute sulphuric acid and ammonium persulphate, and the dioxide either estimated volumetrically, or

[1] Lambert, *Compt. rend.*, 1905, **141**, 357.

in the absence of other metallic salts, gravimetrically by conversion into the red oxide.[1]

Very small traces of manganese can be detected and estimated colorimetrically by adding caustic soda and glycerol, and passing air or oxygen through the solution. A ruby-red coloration is produced and the amount of manganese present can be estimated colorimetrically by comparison with standard solutions of potassium permanganate.[2]

Valuation of Manganese Ores.—The most accurate and convenient methods for the estimation of the quantity of manganese dioxide in manganese ores are those of Bunsen,[3] and of Fresenius and Will.[4] By the former method the quantity of chlorine evolved on treatment with hydrochloric acid is directly determined:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

The free chlorine is collected in a solution of potassium iodide, and the liberated iodine estimated with a dilute solution of sulphurous acid or sodium thiosulphate.

Fresenius and Will's gravimetric method depends upon the fact that when manganese dioxide and oxalic acid are brought together in presence of sulphuric acid, the following decomposition occurs:

$$MnO_2 + C_2O_2(OH)_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

Or 88·00 parts of carbon dioxide correspond to 86·93 parts of manganese dioxide. This is carried out in a weighed apparatus provided with a drying tube, the loss of weight being ascertained.

The Atomic Weight of manganese has been determined by several chemists, among the earliest of whom were Berzelius,[5] Dumas,[6] and V. Hauer.[7] Dewar and Scott, by estimating the percentage of silver in silver permanganate, obtained 55·01;[8] and Marignac, by converting pure MnO into $MnSO_4$, obtained 55·02.[9] Baxter and Hines from the analysis of the bromide and chloride have found 54·96.[10] The value at present (1913) adopted is 54·93.

[1] von Knorre, *Zeit. angew. Chem.*, 1901, **14**, 1149.
[2] Tarugi, *Gazz*, 1906, **36**, i., 332.
[3] *Journ. Chem. Soc.*, 1856, **8**, 219.
[4] *Annalen*, 1843, **47**, 87.
[5] *Pogg. Ann.*, 1828, **14**, 211.
[6] *Annalen*, 1860, **113**, 25.
[7] *Wien. Akad. Ber.*, 1857, **25**, 124.
[8] *Proc. Roy. Soc.*, 1883, **35**, 44.
[9] *Zeit. anal. Chem.*, 1884, **23**, 123.
[10] *J. Amer. Chem. Soc.*, 1906, **28**, 1560.

GROUP VIII.

Sub-group (*a*) Iron, Cobalt, Nickel.
„ (*b*) Ruthenium, Rhodium, Palladium.
„ (*c*) Osmium, Iridium, Platinum.

527 The metals placed by Mendeléeff in the eighth vertical group form a very remarkable feature of his arrangement of the elements. They occur in three sub-groups, each containing three metals, forming the termination of the even horizontal series 4, 6, and 10, each group being the connecting link between the elements of the even series which precedes and those of the odd series which follows. The three metals which make up each horizontal sub-group resemble one another very closely, and differ much less in atomic weight, atomic volume, and general physical properties than is usual in the successive elements of a horizontal series, as may readily be seen by a reference to Lothar Meyer's diagram (p. 60).

This remarkable similarity is borne out by the chemical behaviour of these elements, the various platinum metals, for example, being so similar that their separation from each other is a matter of the greatest difficulty, and this is true also of cobalt and nickel.

At the same time a certain degree of similarity can be traced between those metals which are in the same vertical column, more particularly in sub-groups *b* and *c*. Thus ruthenium and osmium, rhodium and iridium, palladium and platinum agree very closely in many of their most characteristic properties, such, for example, as the formation of a tetroxide, which is peculiar to ruthenium and osmium, &c.

From the analogy of the preceding groups, it would be expected that the characteristic oxide of the metals of this group would have the formula MO_4 or M_2O_8. Actually, however, only ruthenium and osmium form such an oxide, and this is not an acidic oxide, whilst all the metals of the group form lower oxides, many of which correspond to series of stable salts.

All these metals, unlike the other members of the even series of the periodic system, form metallo-organic compounds.[1]

A very characteristic property of the metals of this group is their tendency to form complex radicals with other elements or groups, which then act as basic or acidic radicals, and thus give rise to extended series of compounds. These substances, as a rule, differ entirely in properties from the ordinary salts of the metal, this being due to the fact that each radical has its own characteristic properties, and those of the metal appear only when the radical has been broken up. Some of the most important of these complex derivatives are the double cyanides, such as the ferrocyanides and their analogues, the complex halogen derivatives of the platinum metals, the ammoniacal derivatives of cobalt and of the platinum metals, the double nitrites, sulphites, &c. This tendency is shared by chromium and to some extent by manganese, copper, and other metals which either immediately precede or follow the metals of Group VIII in the periodic system.

SUB-GROUP (*a*). THE IRON GROUP.

Iron, Cobalt, Nickel.

528 These three metals are all magnetic, melt at a high temperature, are oxidised when strongly heated in air or oxygen, and decompose steam at a red heat. They all form basic oxides of the formula $M^{II}O$, and a corresponding series of coloured salts in which the metal is divalent. The sesquioxides $M^{III}_2O_3$ also act as basic oxides, but the corresponding salts of nickel and cobalt are so unstable that they speedily decompose with formation of salts corresponding to the lower oxide. Those of iron, on the other hand, are much more stable, and are formed from those of the lower oxide on exposure to the air. These metals, moreover, all yield oxides of the formula M_3O_4, to which no stable salts correspond, and which are probably to be considered as being themselves salts of the formula $M^{II}M^{III}_2O_4$. Cobalt, in addition to these, probably forms an unstable acidic dioxide, whilst derivatives of the corresponding nickel oxide are also known, but no such derivatives of iron have been prepared, although

[1] Pope and Peachey, *Proc. Chem. Soc.*, 1907, **23**, 86.

the corresponding sulphide exists as iron pyrites. Iron, however, forms a series of compounds known as the ferrates, which are derived from a hypothetical acidic trioxide, FeO_3, to which no analogue is known among the compounds of nickel and cobalt.

Nickel and iron both unite with carbon monoxide to form volatile liquids, whereas cobalt forms a crystalline carbonyl.

Nickel has much less tendency to form complex radicals than cobalt or iron, the most important of such derivatives formed by the last two being the cobaltammines and the cyanogen compounds of iron.

IRON (FERRUM). Fe = 55·84.

529 Iron is the most important of all the metals. It seldom occurs in the metallic state in nature; the ores of iron are, however, found widely distributed, and usually in a state of purity; their reduction to the metal may well be considered as one of the simplest of metallurgical operations, requiring far less knowledge and skill than is needed for the preparation of bronze. In spite of these facts it is usually supposed that the iron age followed those of copper and bronze, although in many cases the art of working in iron became known at a very early period. It is, however, to be remembered that metallic iron is rapidly destroyed by rusting, at any rate in damp situations, and this may to some extent account for the comparatively rare occurrence of very early iron implements.

It appears probable that iron was first obtained from its ores in India, and it is certain that both the Assyrians and the Egyptians employed iron implements many centuries before our era. In the Pentateuch the metal iron is mentioned, as well as the furnaces in which it was prepared; the Hebrew name for iron, Barzél, is derived from the root Bazal which signifies "to be hard," whilst the derivation of the Greek word σίδηρος, which occurs in Homer, is unknown. The Greeks obtained their iron from the Chalybes, a nation dwelling on the south coast of the Black Sea, from whom the Asiatic nations also obtained the metal. The Romans, on the other hand, procured their iron not only from this district, but also from Spain, Elba, and Noricum. The Elban iron mines, which are to this day renowned for their fine specular iron, were worked by the Etruscans, and the method

employed for the extraction of the iron is identical in principle with that still in vogue in the Pyrenees.

The word iron, which is identical with the Scandinavian "iarn" (instead of "isarn"), and with the German "Eisen" (adjective, "eisern"), appears to be connected with the Sanscrit "ayas" (Latin "aes"), and this, according to Grimm, is an indication that bronze was in use among the Germans at a much earlier date than iron. The alchemists connected iron with Mars, the god of war, and gave to it the sign ♂.

Native iron occurs, according to Andrews,[1] in small spiculæ distributed throughout the basalt of the Giant's Causeway, as well as in the old lavas of the Auvergne. The occurrence of terrestrial iron in large lumps has also been observed; these masses have, however, probably been formed in the firing of coal-pits when the burning mass has come in contact with ores of iron; the product is termed natural steel.

The native metal occurs more frequently in the form of *meteoric iron*. The meteorites falling in larger or smaller masses from extra-terrestrial sources may be divided into two groups "Earthy meteorites," which consist chiefly of silicates, and "Meteoric irons," which consist of iron together with a larger or smaller quantity of nickel, the presence of this latter metal being characteristic of meteoric masses.[2] Meteoric iron likewise usually contains small quantities of cobalt and other metals, as well as graphite, ferrous sulphide, and schreibersite, $(Fe,Ni,Co)_3P$, this last compound being one which is not known to exist in any terrestrial mineral. When the surface of a meteoric iron is planed and polished, and then treated with dilute nitric acid, peculiar configurations make their appearance which were first noticed by Widmanstätten in the year 1808. These consist of rhombic folia or crystalline markings (shown in Fig. 187) which have a metallic lustre; the spaces enclosed by these markings are somewhat raised, so that a surface of meteoric iron thus treated may be used as a plate from which an engraving can be obtained. Some meteoric irons do not exhibit these figures, parallel striæ making their appearance when the metal is subjected to a

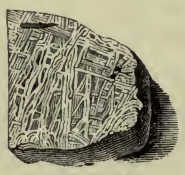


Fig. 187.

[1] Andrews, *Brit. Assoc. Reports*, 1852, 34.

[2] See Fletcher's *Introduction to the Study of Meteorites* (Published by the Trustees of the British Museum, 1904).

similar treatment. Meteoric iron frequently occurs in considerable masses; thus, for instance, that which was discovered by Pallas in Siberia originally weighed 800 kilos. [Analysis (*a*)], whilst that found in Bahia weighed nearly 7,000 kilos.; a still larger mass occurs at Chaco-Gualamba in Peru, which is said to weigh 16,000 kilos., and similar large masses have been found in other localities, both in North and South America, as well as in Africa. The largest known masses are those found at Ovifak on the Island of Disko, off Greenland, where fifteen blocks of meteoric iron occur, the weight of the two largest being, according to Nordenskjöld,[1] 21,000 and 8,000 kilos. [Analysis (*b*)].

The following table gives the composition of several meteoric irons:

	(*a*)	(*b*)	(*c*)	(*d*)
Locality. . .	Siberia.	Ovifak.	Brazil.	Tennessee.
Analyst. . .	Berzelius.	Nordenskjöld.	Damover.	J. L. Smith.
Iron . . .	88·04	84·49	63·69	91·15
Nickel . .	10·73	2·48	33·97	8·01
Cobalt . .	0·46	0·07	1·48	0·72
Copper . .	0·07	0·27	0·05	0·06
Manganese.	0·13	—	—	—
Carbon . .	0·04	10·62	0·02	—
Sulphur .	trace	1·52	0·02	—
Phosphorus	—	0·20	0·05	—
Chlorine .	—	0·72	—	—
Silicate .	0·53	0·09	—	—
	100·00	100·46	99·28	99·94

Finely divided meteoric iron is constantly falling from extra-terrestrial space on to the earth: the occurrence of this meteoric dust has been observed in Sweden and in the snow-fields of Northern Siberia, the snow enclosing black magnetic particles which contain cobalt as well as iron. Similar particles of meteoric dust, consisting of metallic iron, have been found by Murray, of the *Challenger* expedition, at great depths in mid-ocean. It is only under conditions such as the above that it is possible to detect this fine meteoric dust, in consequence of the enormous accumulation elsewhere of terrestrial dust.

530 Iron is usually found in combination either with oxygen or sulphur. Of the large number of minerals which contain iron

[1] *Pogg. Ann.*, 1874, **151**, 154.

only those will now be mentioned which occur most commonly and in the largest quantity; the ores will be specially described hereafter. The most important oxygen compounds of iron are red hæmatite, or specular iron ore, Fe_2O_3; brown hæmatite, $2Fe_2O_3,3H_2O$; magnetic iron ore, Fe_3O_4; spathic iron ore, $FeCO_3$, the latter containing other isomorphous carbonates. Again, iron pyrites, FeS_2, occurs largely, whilst magnetic pyrites, Fe_7S_8, is less common; iron sulphide also forms an important constituent of copper pyrites, $CuFeS_2$, arsenical pyrites, FeAsS, and other minerals. Silicates of iron are found in most geological formations, and from these iron oxide finds its way into the soil, in which it is usually present in considerable quantity, imparting to it a reddish or brown colour. This fact was known to Pliny, who mentions that the presence of iron may be recognised by the colour of the soil. Iron compounds are contained in solution in spring- and river-waters, as well as in the water of the ocean, and it is from one or other of these sources that plants obtain the iron which forms an essential constituent of their chlorophyll.

In 1702 N. Lemery proved that the ashes of plants contained iron: this observation was confirmed by the experiments of Geoffroy in 1705, who, however, assumed that the iron was not originally contained in the plants, but that it was produced when they were burned. Other celebrated chemists, such as Becher, held the view that the iron which made its appearance when certain substances were subjected to chemical treatment was not contained in them, but was produced independently. This erroneous opinion was first disproved by Lemery.

Iron likewise is a necessary constituent of the animal body; for instance, hæmoglobin, the red colouring matter of the blood, contains 0·336 per cent. of iron. Iron preparations have also long been employed as medicine, especially in anæmia. After the use of iron the number of red corpuscles is increased, and the amount of hæmoglobin which they contain becomes larger. The presence of iron in the blood was first shown by Menghini of Bologna in 1747.

The existence of iron in large quantities in meteoric masses indicates a wide cosmical distribution of the element, and this conclusion has been confirmed by Spectrum Analysis, which indicates the presence of iron in the sun and many fixed stars.

531 *Preparation of Pure Iron.*—Iron is usually produced from its oxides by reduction with carbon, and is thus obtained on the

large scale; thus prepared, however, iron is not pure, but contains more or less carbon. The purest commercial form is wrought iron, especially the finest kinds of piano-wire: this contains about 0·3 per cent. of foreign impurities, consisting chiefly of carbon. In order to obtain chemically pure iron, the oxide, or oxalate, may be heated in a current of hydrogen at the lowest possible temperature; the metal is obtained by this process as a black powder which oxidises and becomes incandescent in the air; if the reduction is carried on at a higher temperature the powdered iron is not pyrophoric. Reduction of the oxide or basic nitrate by hydrogen at 1000° gives a product with a distinct metallic lustre and a light grey colour.[1]

Pure iron may be prepared also by electrolysis, the best conditions for obtaining thick homogeneous deposits being the following.[2] A bath is made up containing 200 grams of ferrous chloride or ferrous ammonium sulphate, 50 grams of magnesium sulphate, and 5 grams of sodium hydrogen carbonate per litre, and electrolysed with a current density of 0·003 ampere per sq. cm. at the cathode. The latter is of copper, thinly silvered and iodised, and maintained in rotation, whilst the anode is of wrought iron. More sodium hydrogen carbonate is added from time to time as the electrolysis proceeds. The iron formed improves in quality as time goes on, and finally reaches a strength of 5,180 kilos. per sq. cm., and may be bent at a sharp angle without breaking. Owing to the low current density, the iron formed is free from occluded hydrogen, which is always present in electrolytic iron deposited with a high current density.

Properties.—Pure iron has a specific gravity of 7·86, possesses an almost silver-white lustre, and takes a high polish; it is, with the exception of cobalt and nickel, the most tenacious of all the ductile metals at the ordinary temperature, but becomes brittle at the temperature of liquid air.[3] Its average specific heat over 15–100° C. is 0·10983, but this increases somewhat rapidly with the temperature up to 850°, after which it decreases.[4]

[1] Lambert and Thomson, *Journ. Chem. Soc.*, 1910, **97**, 2430.

[2] Maximowitsch, *Zeit. Electrochem.*, 1905, **11**, 52; Ryss and Bogomolny, *ibid.*, 1906, **12**, 697. Compare Amberg, *ibid.*, 1908, **14**, 326; 1910, **16**, 125; Müller, *Metallurgie*, 1909, **6**, 145: Pfaff, *Zeit. Elektrochem.*, 1910, **16**, 217.

[3] Dewar and Hadfield, *Proc. Roy. Soc.*, 1905, **74**, 326.

[4] Harker, *Phil. Mag.*, 1905, [6], **10**, 430.

Pure iron becomes soft at a red heat, and may be readily welded at a white heat, but above the welding point it becomes brittle under the hammer. It fuses less readily than commercial wrought iron, the melting point being 1505–1520°,[1] and when heated in the electric furnace it readily distils, much frothing taking place in the boiling liquid owing to the evolution of occluded gases.[2] It is attracted by the magnet and may also be rendered magnetic, but loses this property rapidly. Carbonised iron or steel, on the other hand, retains its magnetic property at the ordinary temperature, but loses it at a red heat.

When iron is heated from the ordinary temperature to the melting point it undergoes two changes, the first taking place about 760° and coinciding with the disappearance of magnetic properties, and the other occurring at 900° (see also p. 1215). Osmond and Cartaud[3] conclude, therefore, that iron exists in three allotropic forms, distinguished as α-, β-, and γ-iron, or α-, β-, and γ-ferrite, the last being stable above 900°, and usually formed on the solidification of the fused metal, whilst the α-form is the sole constituent of pure soft iron and is capable of assuming magnetic properties. All three forms crystallise in the regular system.

Iron combines readily with the elements of the chlorine group, and when strongly heated burns in oxygen, forming the magnetic oxide, and at a red heat decomposes steam with formation of the same oxide; it also burns at a red heat in sulphur vapour, and combines with carbon at a high temperature. Hence all the iron obtained on the large scale contains carbon in combination; the larger the quantity of this element it takes up, the more readily fusible is the iron.

Iron dissolves in most dilute acids with evolution of hydrogen. Dilute nitric acid dissolves it in the cold without the evolution of any gas and with the formation of ferrous nitrate, $Fe(NO_3)_2$, and ammonium nitrate; when heat is applied, or when a stronger acid is employed, oxides of nitrogen are evolved, and ferric nitrate, $Fe(NO_3)_3$, is formed.

Passive Iron.—When iron is placed in concentrated nitric acid it appears to undergo a change, and is then not attacked by the acid, nor will it then precipitate metals, such as

[1] See Carpenter, *J. Iron Steel Inst.*, 1908, **78**, 290.

[2] Moissan, *Compt. rend.*, 1906, **142**, 425.

[3] *Ann. des Mines*, 1901, **17**, 110; **18**, 113; *Compt. rend.*, 1906, **142**, 1530; **143**, 44.

copper, from solutions of their salts. Iron in this state is termed "passive."[1] This condition may be brought about by the action not only of nitric acid, but also of other substances such as chloric, bromic, iodic, and chromic acids, and even hydrogen peroxide, as well as by electrolysis, the iron acting as anode in sulphuric acid solution.

The cause of this phenomenon has not yet been definitely ascertained. Faraday and Beetz regarded it as due to the formation of a thin film of oxide on the surface of the iron, which protects it from further action, and this film, according to Haber and Goldschmidt,[2] possesses metallic conductivity.

Fredenhagen[3] supports the hypothesis that in the passive condition the iron is coated with a thin layer of gas, and points out that iron rendered passive by anodic polarisation has a different behaviour from that made passive by nitric acid, probably because the protective layer is oxygen in the one case, and an oxide of nitrogen in the other. Hittorf,[4] Heathcote,[5] and Finkelstein,[6] on the other hand, regard the phenomenon as due to a chemical or electrical change taking place in the molecules forming the surface of the iron, the last-named author suggesting that ordinary iron consists of both ferrous and ferric iron molecules, and that by the action of the above substances the ferrous iron molecules are dissolved or converted into ferric molecules, which are not capable of attack by the reagents.

Finely Divided or Reduced Iron (ferrum redactum) has long been used in medicine. *Spongy iron*, prepared by the reduction of burnt pyrites or other suitable iron ore, has been employed as filtering material for purifying water for domestic use.

532 *The Rusting of Iron in the Air.*—The formation of rust on exposed surfaces of the metal was formerly supposed to be due to direct oxidation of the metal. Experience showed, however, that contact with both air and water in the liquid state is necessary for the production of rust. The investigations of

[1] Keir, *Phil. Trans.*, 1790, **80**, 359.

[2] *Zeit. Elektrochem.*, 1906, **12**, 49; see also Gordon and Clark, *J. Amer. Chem. Soc.*, 1906, **28**, 1534; Byers, *ibid.*, 1908, **30**, 1718; Krassa, *Zeit. Elektrochem.*, 1909, **15**, 490; Dunstan and Hill, *Journ. Chem. Soc.*, 1911, **99**, 1853; Flade and Koch, *Zeit. Elektrochem.*, 1911, **18**, 335.

[3] *Zeit. physikal. Chem.*, 1903, **43**, 1; 1908, **63**, 1.

[4] *Zeit. physikal Chem.*, 1900, **34**, 385.

[5] *Zeit. physikal Chem.*, 1901, **37**, 368; *J. Soc. Chem. Ind.*, 1907, **26**, 899.

[6] *Zeit. physikal Chem.*, 1902, **39**, 91.

Crace-Calvert [1] and Crum Brown [2] showed that the reaction is not one of direct oxidation, but that the carbonic acid of the air plays an essential part in the reaction. The feebly acid solution of the latter in water attacks the iron with considerable rapidity, yielding a solution of ferrous carbonate in excess of carbonic acid, which is then oxidised by the oxygen of the air with formation of hydrated ferric oxide and evolution of carbon dioxide :

$$Fe + H_2O + CO_2 = FeCO_3 + H_2$$
$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2.$$

The correctness of this explanation was called in question by Dunstan, Jowett, and Goulding,[3] who suggested that the presence of carbonic acid is not necessary, but that the iron acts on the oxygen of the air and water with formation of ferrous oxide and hydrogen peroxide, and that these two substances then interact with formation of hydrated ferric oxide :

$$Fe + O_2 + H_2O = FeO + H_2O_2, \qquad 2FeO + H_2O_2 = Fe_2O_2(OH)_2,$$

the excess of hydrogen peroxide immediately reacting with iron to form a further quantity of rust. No evidence of the intermediate formation of hydrogen peroxide has been found, the authors basing their conclusion mainly on the fact that substances which destroy hydrogen peroxide appear also to prevent rusting. Moody [4] has, however, shown that when carbonic acid, and also all other dilute acids (which act in the same manner as carbonic acid), are absolutely excluded, water and oxygen are incapable of bringing about the formation of rust, and further that freshly formed rust always contains considerable quantities of ferrous hydroxide and carbonate, which could not be the case if the hydrogen peroxide theory were correct. Moreover, he finds that previous to the formation of the rust the iron passes into solution in the water, the rust being secondarily produced by the oxidation of the dissolved iron, which is in full accordance with the Crace-Calvert hypothesis but in contradiction to that of Dunstan, Jowett, and Goulding.[5]

[1] *Mem. Manch. Phil. Soc.*, 1876, **5**, 104.

[2] *J. Iron Steel Inst.*, 1888, ii , 129.

[3] *Journ. Chem. Soc.*, 1905, **87**, 1548 ; *Proc. Chem. Soc.*, 1907, **23**, 63.

[4] *Journ. Chem. Soc.*, 1906, **89**, 720 ; *Proc. Chem. Soc.*, 1907, **23**, 84.

[5] See also Walker, Cederholm, and Bent, *J. Amer. Chem. Soc.*, 1907, **29**, 1251 ; Tilden, *Journ. Chem. Soc.*, 1908, **93**, 1356 ; Friend, *J. Iron Steel Inst.*, 1908, **77**, 5 ; Lambert and Thomson, *Journ. Chem. Soc.*, 1910, **97**, 2426 ; Dunstan and Hill, *ibid*, 1911, **99**, 1835 ; Andström, *Zeit. anorg. Chem.*, 1910, **69**, 10 ; Lambert, *Journ. Chem. Soc.*, 1912, **101**, 2056.

The formation of rust takes place to begin with but slowly, but as soon as a thin superficial layer of rust has formed, the process goes on rapidly. Certain salts, especially those of ammonia, promote the oxidation, whilst the liability to rusting is diminished by the presence of alkalis, as these prevent the formation of any free carbonic acid. Steel instruments may be kept bright by immersion in a solution of caustic soda or, better, of sodium nitrate. In order to lessen the liability to rust, iron articles are coated with varnish or oil-paints, or the surface is covered with oil, grease, or graphite. A coating of magnetic oxide of iron, Fe_3O_4, is, however, the most efficient protective, and to obtain such a coating articles of iron are subjected to the action of superheated steam at a temperature of about 650°, this process being known, from the name of its inventor, as the Barff process.

In contact with zinc, iron becomes electronegative and is thereby to a considerable extent prevented from rusting. Iron articles are therefore often covered with a coating of zinc (galvanised iron), and also with tin (tin-plate), and nickel, to protect them from atmospheric action.

533 *Iron amalgam* does not form readily, but on acting with a 1 per cent. sodium amalgam upon a solution of ferrous sulphate, a semi-solid mass is obtained which, when in small globules, is attracted by the magnet. On distilling this amalgam, metallic iron remains in a state of fine division (Böttger). The same amalgam can be formed by rubbing powdered iron with mercuric chloride and water. If an iron wire be attached to the copper pole of a Daniell element, and dipped into a solution of ferrous sulphate, whilst another iron wire from the zinc pole touches a drop of mercury lying in the solution, amalgams of varying composition are obtained according to the intensity of the current. Those containing only small quantities of iron are liquid; those in which more iron is present are soft and crystalline. One containing 103·2 of iron to 100 of mercury forms a hard black mass, and is obtained by submitting the liquid amalgam to a pressure of 50 tons to the square inch.

[1] Joule, *Journ. Chem. Soc.*, 1863, **16**, 378.

METALLURGY OF IRON.[1]

534 Several mythical stories point to the fact that in very early times meteoric iron, which, falling from the heavens, was considered as a gift of the gods to man, was employed in the manufacture of iron weapons. Kumbary[2] relates that the chiefs in the Wadai country, in Central Africa, possess many weapons which have been worked up from meteoric masses. But meteoric iron occurs so sparingly upon the earth's surface, and is, in fact, so unsuited to the manufacture of tough forgings, that at a comparatively early period in the history of civilisation men set about the smelting of iron from its ores.[3]

The enormous deposits of ancient slag and furnace-cinder which are found spread over large areas in various districts of India point to the fact that the iron industry existed in that country at very early times, and even to the present day the manufacture of iron is carried on in India in the most primitive manner. It is also clear that the ancient Assyrians and Egyptians were well acquainted with the uses of iron, and the remains of their iron works have been found near Sinai. But, independently of these sources, a knowledge of the methods of working iron ores also appears to have been gained by the tribes living in the North of Europe, whilst the inhabitants of the Western Hemisphere were not acquainted with these processes. Little is known respecting the method employed by the ancients in the manufacture of iron; the slight information which we possess has been collected together by Agricola in his works, "De Veteribus et Novis Metallis," and "De Re Metallica."[4] The apparatus employed was evidently of a primitive kind, and consisted of a small hearth or furnace to which was attached a bellows or blowing arrangement driven by hand, similar indeed to that which is now in use among the hill-tribes in India and in Central Africa. Malleable iron and steel are both produced by igniting the iron ore with charcoal, the metal being obtained in the form of a porous lump or "bloom," which was pressed or hammered into a coherent metallic mass.

[1] Further information on this subject may be obtained from the metallurgical works of Percy, Turner, Howe, Harbord, Sexton, and Carnegie.

[2] *Compt. rend.*, 1870, **70**, 649.

[3] See "The Early Use of Iron," Brough, *J. Iron Steel Inst.*, 1906, **69**, 233.

[4] See the translation from the Latin Edition of 1556, by H. C. Hoover and L. H. Hoover; published by *The Mining Magazine*, 1912.

The dexterity exhibited by the Hindoos in the manufacture of wrought iron may be estimated from the fact of the existence in the Mosque of the Kutub near Delhi of a wrought iron pillar no less than 24 feet in length.[1] This pillar stands about 22 feet out of the ground, and has an ornamental cap bearing an inscription in Sanskrit belonging to the fourth century. An analysis of specimens obtained from the actual pillar by Hadfield shows that the material is an excellent type of wrought iron, made with a very pure fuel, probably charcoal.

Cast Iron, Wrought or Malleable Iron, and Steel.

535 The iron which is obtained from its ores by metallurgical processes is never pure, but invariably contains other constituents, which greatly affect the properties of the metal, and determine its value for various purposes. The most important of these additional constituents are carbon, silicon, phosphorus, sulphur, and manganese, and in special cases, nickel, chromium, tungsten, vanadium, aluminium, and molybdenum. It is found that comparatively small variations in the amount of these substances which are present exert an enormous influence on the properties of the metal.

Four main varieties of commercial iron are usually distinguished:

(1) *Cast iron* contains 2·2–4·5 per cent. of carbon, besides varying quantities of the other elements mentioned above. This variety fuses readily, and when cold is brittle and cannot be worked under the hammer.

(2) *Wrought* or *malleable iron* contains little carbon and fuses with difficulty, but is malleable and can therefore be worked under the hammer, and can be welded at a red heat. The characteristic feature of malleable iron is that it is produced in a pasty state without having been melted, and consequently contains particles of slag, which cannot be completely removed from the unfused metal.

(3) *Steel* comprises all malleable alloys of carbon and iron which have at any time been actually melted. It contains very

[1] A cast of this pillar was formerly to be seen in the Architectural Court of the South Kensington Museum, but was destroyed during a fire in 1885. A drawing of the pillar is found in St. John Day's *Prehistoric Use of Iron and Steel*, p. 144, and a reproduction from a photograph in the *J. Iron Steel Inst.*, 1912, **85**, 168, Plate 14.

little slag, but otherwise does not necessarily differ in composition from malleable iron. Steel possesses the valuable property of becoming hard when it is suddenly cooled from a high temperature, the intensity of this effect depending upon the amount of carbon which it contains.

(4) *Special steels* contain, besides carbon, varying quantities of one or more of the following elements: manganese, nickel, chromium, tungsten, silicon, vanadium, molybdenum, and aluminium. Some of these have valuable mechanical and magnetic properties not possessed by ordinary carbon steels.

The general process of iron smelting consists essentially in the removal of the oxygen from the ores, and this is invariably carried out in practice by the action of carbon at a high temperature. In addition to the oxygen, the extraneous matter contained in the ore, such as silica, alumina, sulphur, phosphates, &c., must also be removed, and the resulting iron must be exposed to such conditions that it acquires the composition which will fit it for the special purpose to which it is to be applied.

Ores of Iron.

536 The term iron ore includes only those minerals which contain iron both in sufficient quantity and also in a condition which enables them to be employed for the economic production of the metal. Thus, for example, iron pyrites, FeS_2, although it occurs in very large quantities and contains a high percentage of iron, cannot properly be described as an iron ore, inasmuch as it is difficult to remove the sulphur completely, a small proportion of which renders the metal unfit for use. In like manner arsenical pyrites, although it also contains a large quantity of iron, is unfit for the production of the metal; and the same may be said of many other minerals which contain large quantities of iron.

The various ores of iron are composed of, or yield, the oxides of iron in more or less pure condition, and the value of an iron ore is influenced rather by the nature of the impurities which it contains than by its percentage of iron.

The ores of iron occur in almost every geological formation; thus magnetic iron ore is found in the older rocks, as in the laurentian beds of North America, and the old slates and gneisses of Sweden, whilst red hæmatite occurs in beds or pockets in the carboniferous limestone of Cumberland and

North Lancashire, and spathic or clay iron stone in the coal measures. Again, the oolitic rocks furnish large deposits of brown hæmatite, and the Elba ore is probably a tertiary deposit. Still more recent formations of iron ore are seen in the bog ore of Germany and the North of Ireland, whilst "lake ores" are being formed in Scandinavia at the present day.

Magnetic Iron Ore, Magnetite, or *Loadstone,* Fe_3O_4.—This ore, in the pure state, constitutes the richest ore of iron, containing 72·4 per cent. of the metal. It occurs in the crystalline and massive state as well as in the form of sand, and is found in large deposits, especially in volcanic rocks, as well as in granite, gneiss, and mica-schist. The most important localities of magnetite are Arendal, Dannemora, and other places in Norway, Sweden, and Lapland; the island of Elba; the Ural Mountains; and several localities in the United States, especially near Lake Superior. In England magnetic oxide of iron occurs on Dartmoor, at Brent in South Devon, and at Treskerby in Cornwall; but it cannot be said to be an important English ore. In Germany it is found in large quantities at Schmiedeberg, in Silesia, and a few other localities.

Franklinite, $(Fe,Mn)_2O_3,(Fe,Zn)O$, occurs in New Jersey, and is first worked for zinc, the residue being used as an iron ore for the production of spiegeleisen.[1]

Red Hæmatite, or *Specular Iron Ore,* Fe_2O_3. — This substance occurs crystalline as specular iron ore, and also in a massive state having a columnar, granular, or botryoidal form, as well as in the earthy condition. This ore, being free from impurities, yields a cast iron which is especially well adapted for the manufacture of malleable iron and steel. Hæmatite occurs in veins as well as in beds and pockets. One of its most remarkable localities is the island of Elba, where it occurs finely crystallised between talcous schist and crystalline limestone. The Elba mines were worked by the Etruscans, and are still productive. A fine hæmatite occurs in the Huronian rocks on the southern shore of Lake Superior, whilst at Iron Mountain, near St. Louis, Missouri, enormous masses of this ore of iron are found. On the continent of Europe hæmatite occurs in Belgium, and deposits of this ore are found also in the Devonian formation on the Lahn in Westphalia. The chief deposits of hæmatite in England are those near Ulverston in Lancashire, and on the coast of Cumberland

[1] *J. Iron Steel Inst.*, 1894, **45**, 416.

near Whitehaven; the ore here occurs in beds or pockets in the carboniferous limestone, sometimes existing as hard botryoidal masses exhibiting crystalline structure, and sometimes in a soft or compact amorphous condition.

Brown Hæmatite, or *Limonite*, $Fe_2O_3,2Fe(OH)_3 = 2Fe_2O_3,3H_2O$. —This substance occurs crystallised in rhombic prisms, but is more frequently found either in a fibrous foliated and scaly condition, or as a dark brown reniform mass and commonly known as Brown and Yellow Hæmatite. In the massive state this ore occurs in large quantity, and, as it can be readily worked, it has been long employed as a source of iron (for analysis see table on p. 1177). It is found in the carboniferous limestone as well as in the older rocks, in the Forest of Dean, and at Llantrissant in Glamorganshire in the lower coal measure sandstones. At Bilbao in Spain it occurs largely in the carboniferous limestone, whilst the newer and earthy brown hæmatite is found in the oolite and greensand in Northamptonshire and Lincolnshire. It is likewise largely worked in Germany and France, being the ore from which the greater part of the iron made in these countries is derived. The bog ores which are worked in the plains of North Germany and Canada and in other places, as well as the peculiar iron ore of the North of Ireland and the Swedish lake ore, belong to this class, and are of the most recent geological formation.

Spathic Iron Ore, or *Siderite*.—Spathic iron ore consists of ferrous carbonate, $FeCO_3$, invariably mixed with the isomorphous carbonates of manganese, magnesium, and calcium. It possesses a yellowish-brown colour, and occurs often in globular or botryoidal forms having a silky fibrous structure. It is usually found in Devonian rocks, occurring in England at Brendon Hill in Somerset, on Exmoor, and at Weardale in Yorkshire.

Clay Iron-stone, or *Argillaceous Iron Ore*, is a spathic iron containing clay, and is chiefly found in nodules or bands interspersed throughout the clays and shales of the coal measures. This ore is the most important English ore of iron. The chief workable beds of British clay iron-stone occur in Yorkshire, Derbyshire, Staffordshire, Warwickshire, South Wales, and Scotland.

The "black band" iron-stone is an important variety of this ore. It contains from 20 to 25 per cent. of carbonaceous matter, and is found in Lanarkshire, North Staffordshire, and South Wales. The Scotch beds were discovered by Mushet in 1800,

but they were not worked until the year 1830. In 1855 the same ore was discovered in Westphalia, and it is worked also in Lower Silesia. The coal measures of the Gard and of the Aveyron in France, and those in Pennsylvania and Maryland and other States, also contain large quantities of clay iron-stone. The same ore is found in strata in the lias and also in the oolitic and tertiary rocks, the Cleveland iron ore belonging to this last class. Analyses of some clay iron-stones are given on p. 1177.

Calcination of the Ore.

537 Before treatment in the furnace many iron ores, especially the clay iron-stones and the brown hæmatites, are subjected to a process of calcination or roasting. The object of this is to expel water and carbonic acid, and also to render the ore more porous, and thus to facilitate the subsequent reduction to metal. At the same time any sulphides which the ore may contain are oxidised and the sulphur expelled. The ordinary clay iron-stone is sometimes roasted in large open heaps, the ore being mixed with a sufficient quantity of coal to keep up a slow combustion. A preferable method is to calcine the ore in kilns or roasters, as in these the consumption of fuel is less and the product more uniform than in the ruder process of roasting in heaps.

The Manufacture of Cast Iron.[1]

538 The application of the blast furnace to the manufacture of iron marks an era in the history of the iron industry, inasmuch as it was by its use that a continuous process of iron manufacture became possible. The discovery of a process by which fusible cast iron can be prepared appears to have been made, probably accidentally, about the end of the fifteenth century, in Germany, where the Stückofen had long been in use for manufacturing blooms. No description of the process is, however, to be found in the older writers upon metallurgy. Thus Agricola, writing in 1556, mentions only the older methods of iron making, although he appears to have been acquainted with cast iron; at any rate the new method must have been at work in this

[1] For further interesting information on this subject the reader is referred to Percy's admirable "Sketch of the History of Iron," *Iron and Steel*, p. 873, and to Turner's *Metallurgy of Iron*, 1 *et seq.*

Analyses of the Chief Ores of Iron.

	Magnetic Iron Ore.	Red Hæmatite.	Brown Hæmatite.		Spathic Iron Ore.	Clay Iron-stone.	
	Sweden.	Ulverston.	Forest of Dean.	Spain.	Erzberg.	Lowmoor.	Cleveland.
Ferrous oxide . . .	28·42	—	—	—	55·64	36·14	39·92
Ferric oxide	62·06	86·50	90·05	78·80	—	1·45	3·60
Manganous oxide . .	—	0·21	0·08	0·65	2·80	1·38	0·95
Alumina	—	—	trace	3·50	—	6·74	7·86
Lime	—	2·77	0·06	trace	0·92	2·70	7·44
Magnesia	1·44	1·46	0·20	trace	1·77	2·17	3·82
Alkalis	—	—	—	—	—	0·65	0·27
Carbonic acid . . .	—	2·96	—	—	38·35	26·57	22·85
Sulphur trioxide . .	—	0·11	trace	—	—	—	—
Iron sulphide . . .	0·07	—	—	—	—	0·10	0·11
Phosphoric oxide . .	—	trace	0·09	0·07	—	0·34	1·86
Silica	7·60	6·55	1·07	5·55	—	17·37	7·12
Insoluble matter . .					—	—	—
Water	—	—	9·22	11·65	—	1·77	2·97
Organic matter . .	—	—	—	—	—	2·40	1·64
Total	99·59	100·56	100·77	100·22	99·48	99·78	100·41

country in 1543, for we find that in that year English cast iron cannons were used. The great demand for cast iron, which was of course all made with charcoal, soon leading to a destruction of our forests, it became necessary, in the first year of the reign of Elizabeth, to endeavour to replace charcoal by some other fuel. This was accomplished by the employment of coke instead of charcoal, a practice which was carried out in England by Dudley as early as the first half of the seventeenth century, but which afterwards fell into abeyance. It was subsequently revived by Abraham Darby at Colebrookdale, about the year 1735.

The blast furnace consists of a shaft varying in height from 50 to 100 feet, the largest diameter being 14 to 24 feet. The essential parts of the furnace are, first, the hearth or crucible, and, second, a shaft or chimney formed of two truncated cones joined at their bases, the upper being termed the "body" and the lower one the "boshes." Fig. 188 shows the construction of such a furnace on the scale of 1 : 180.

The shaft, A Fig. 188, is 75 feet high, the diameter at the widest part (the belly or bosh) being 20 feet, whilst at the throat, B, it is 16 feet, and at the hearth, C, 11 feet. The shaft is constructed of an outer shell of wrought iron or mild steel plates, supported by means of cast iron columns, D, and is lined with fire-brick. In the lining of the boshes, which is exposed to the highest temperature, cooling boxes are inserted in many furnaces. These consist of narrow flat boxes made of gun-metal, which are built into the brickwork, and are cooled by a current of water, thus preventing the brickwork from becoming too hot. The wall of the hearth, which is also lined with fire-brick, is pierced by several openings; the tapping hole, E, by means of which the molten iron is periodically withdrawn; the slag-notch (not shown in the diagram), which is situated at a higher level, and through which the lighter slag is constantly allowed to flow away into trucks or ladles; and, finally, the openings by which the blast of air is introduced through the tuyères.

The throat of the furnace is closed by a contrivance known as the cup and cone arrangement, first introduced by G. Parry at the Ebbw Vale works in 1850. It consists of a cast iron funnel, fixed at the mouth of the furnace, and closed by a cast iron cone, suspended at one end of a counterpoised lever, or by means of a chain and wheel. The charge is tipped from barrows on to

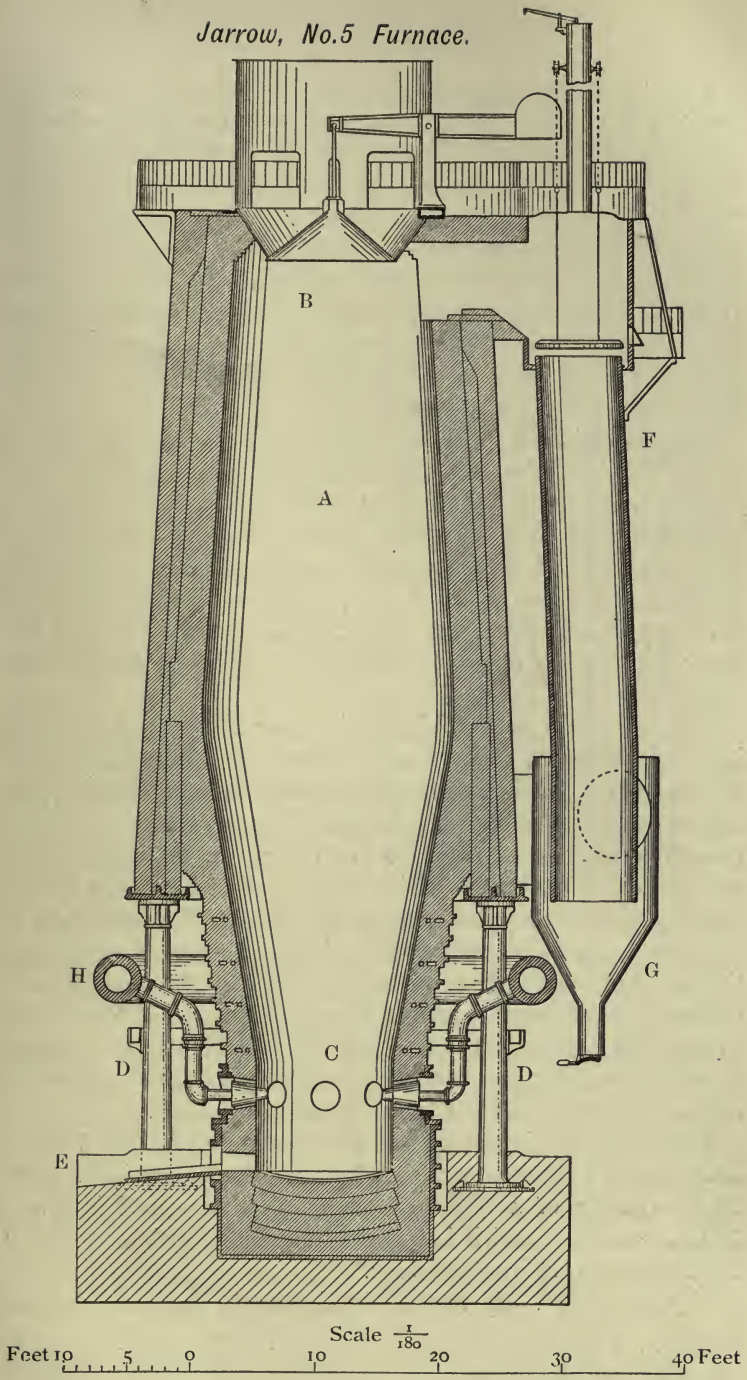

Jarrow, No.5 Furnace.
B
A
F
G
H
D
C
D
E
Scale 1/180
Feet 10 5 0 10 20 30 40 Feet

FIG. 188.

the cone, and is introduced into the furnace by momentarily lowering the latter. When the cone is raised against the funnel (as shown in the figure) the throat of the furnace is closed, and the escape of gases into the air prevented; these then pass out of the furnace by the downcast, F, Fig. 188, which is provided with a dust-catcher, G, and are then usually conveyed through the main to the stoves for heating the blast, to the boilers, or to any other point where the heat produced by their combustion can be made available. Great developments are being made in the direct use of this gas for raising power in gas engines.[1]

The blast of air is introduced near the bottom of the furnace through tuyère holes, perforating the walls of the hearth. The tuyères are made of wrought iron, cast iron, or bronze, and have a double casing through which water circulates to keep them cool: they vary in number from 8 to 16 according to the size of the furnace, are about 5 to 7 inches in diameter, and are fed from an annular pipe, H, Fig. 188, which surrounds the lower part of the furnace, and is connected with the blowing engine.

Hot and Cold Blast.—Up to the year 1828 air was blown into the furnace at the ordinary atmospheric temperature, but in that year J. B. Neilson[2] patented a process for heating the air before it passed into the forge or furnace, and this process, inasmuch as it saved from 15 to 25 per cent. of the fuel, and was also accompanied by an increased productive power of the furnace, was soon generally adopted, although the cold blast is still employed in certain works. For the purpose of heating the air, the waste gases from the furnace are burned in a Cowper's or Whitwell's stove or some modification of these, such as the Massick and Crookes, the Ford and Moncur, or the Cowper-Kennedy; all these act on the principle of the Siemens regenerator, and raise the temperature of the blast.

The air is thus introduced at a temperature of about 700° to 800°, and at a pressure of about 5 lbs. to the square inch. The total capacity of a furnace such as that described is about 14,150 cubic feet, and it is capable of producing about 1,000 to 1,300 tons of cast iron per week.

Dry air Blast.—A recent development in blast furnace

[1] Hubert, Reinhardt, and Westgarth on Blast-furnace Gas Engines, *J. Iron Steel Inst.*, 1906, **71**, 16—168.

[2] Patent No. 5701, March 3rd, 1828.

practice is the drying of the air before passing it through the stoves.[1] This is accomplished by drawing the air through refrigerators in which the moisture is collected. By this means it is claimed to be possible to increase the burden and production of pig-iron by 20 per cent., to reduce the amount of coke per ton of iron by 18 per cent., and to diminish the duty on the blowing engines on account of the colder air being denser. The greatest advantage is, however, in the regularity of working the furnace, because the amount of moisture carried into the furnace by the blast varies very largely from day to day with change of atmospheric conditions, so that the burden of the furnace must have a safe margin of fuel to allow of a sudden loss of heat due to this cause.

539 *The Working of the Furnace.*—For the purpose of starting the newly-built blast furnace it is necessary that the whole should be gently heated by means of a small fire, usually made by piling a quantity of rough dry timber in the hearth, on to the top of which charges of coke are placed. As soon as the shaft has become warm, regular charges of calcined iron-stone, limestone, and coke are added, until the furnace is filled. The blast is then turned on to about one-fifth of the quantity usually employed, the size of the tuyères being so gradually increased that it is not until the furnace has been in blow for from four to five weeks that the full-sized pipes are used, and several months generally elapse before the furnace is in full work.

The proportion of the materials employed, viz., iron ore, limestone or lime, and fuel, termed the *charge* or *burden*, varies considerably according to the nature of the ore. If it be siliceous or clayey, the proportion of lime added must be increased; whilst if the ore contain lime instead of silica, the addition of silicates may be requisite. The object of these additions is to form fusible slags, so that the impurities of the ore may be removed and the furnace kept open and in proper working. The slag consists of calcium and aluminium silicates, and it is extremely important that it be kept of the right basicity and fusibility. If the supply of lime and alumina be insufficient to combine with the silica present, oxide of iron passes into the slag, thus causing waste, whilst if an excess of these bases be used the lining of the furnace is attacked. The fusibility of

[1] Gayley, *J. Iron Steel Inst.*, 1904, **66**, 274; 1905, **67**, 256; see also Daubiné and Roy, *J. Iron Steel Inst.*, 1911, **83**, 28.

the slag moreover determines the temperature which can be reached, and is therefore of great importance, as this has a great effect on the nature of the iron produced. The higher the temperature which is required for the reduction of the ore the less fusible must be the slag. As soon as the proper proportions between the fuel, ore, and limestone have been ascertained, it is of the greatest importance that these proportions should be strictly adhered to, and for this purpose the charges are regularly weighed, and supplied in alternate piles at the top of the furnace, into which they are charged by lowering the cone as already described.

On the average about one ton of coke and 8 to 12 cwt. of limestone are required for each ton of iron produced, about 5 tons of heated air being used in the operation. When the furnace is in regular blast, a constant stream of slag passes out from the slag-hole, the iron collecting in the lower part of the hearth, and being from time to time tapped by piercing a plug of sand and clay by which the tap-hole has been closed. Before tapping, moulds are prepared for holding the metal; these are formed in the sand as a series of parallel trenches, which are placed in communication with the tap-hole. The blast of air is then shut off, and the tap-hole opened by piercing the plug with a long bar of iron. The melted iron flows into the channels communicating with the moulds and assumes the form of semi-cylindrical bars or "pigs" united to one another by one of larger dimensions termed the "sow."

If, owing to some accident to the machinery, a blast furnace is obliged to stand when hot, the operations may be suspended for several months if the throat and tuyère-holes are closed up with sand or clay. Should, however, serious damage have occurred, the furnace must be "blown out." This is accomplished by reducing the burden, and thus increasing the temperature for a time so as to remove any aggregations of solid matters which are fusible only at a high temperature. Finally only fuel is charged, the contents of the furnace are allowed to burn out, and the last tapping is made at a point as low down in the hearth as possible. The life of a blast furnace varies considerably, lasting from five to twelve years, or even for a longer time, according to circumstances.

The size and shape of blast furnaces have been and continue to be very different. When charcoal is employed, as was formerly universally the case, and is still so in countries where

wood is plentiful, the furnace is usually only from 20 to 30 feet in height. The charcoal iron which is thus manufactured in Sweden, Russia, and America is especially valuable for the preparation of fine iron wire, and of the best kinds of steel. Blast furnaces in which the fuel used is either coke, anthracite, or ordinary coal, are, on the other hand, of much larger dimensions, the exact height and capacity of the furnace being regulated by the nature and amount of iron which has to be produced, as well as (it may be added) by the ideas of the ironmaster.

In the year 1750 each English blast furnace produced about 300 tons of pig-iron per annum, whereas a large-size modern furnace yields up to 70,000 tons in the same period. In the Cleveland district, where the blast furnaces are unusually large, the average capacity of those built up to the year 1854 was about 7,000 cubic feet; whilst those built during the years 1870 and 1871 have an average capacity close upon 30,000 cubic feet; in some cases, however, the height rises to 105 feet, and the capacity to 50,000 cubic feet. The production of a blast furnace increases, of course, with its size, but not in a direct ratio; thus Lowthian Bell has shown that an old furnace of 1853, having a capacity of 6,000 cubic feet, yielded one ton of iron per twenty-four hours for every 190 cubic feet of space; whilst in the high furnace built in 1870, 380 cubic feet of space are required to produce one ton of iron in the same time: hence the maximum limit of economic action may be passed by increased size. At the present time in England somewhat smaller furnaces are again being built.

The maximum production is at present gained in America, where large furnaces, running up to about 75 to 90 feet in height, are employed, and the blast is fed at a higher pressure, averaging about 10 lbs. to the square inch. The furnace thus works more rapidly, producing as much as 100,000 to 150,000 tons per annum.[1]

540 *Chemical Changes in the Furnace.*—A large number of investigations have been made on the subject of the changes which occur in the blast furnace, but in spite of these our knowledge of them is still far from complete. The fuel at the hearth, uniting with the oxygen of the blast, which is insufficient for its complete combustion, burns with formation of carbon monoxide. This gas, coming into contact with the con-

[1] One of the Carnegie Steel Company's furnaces produced 918 tons of pig iron in twenty-four hours on March 30th, 1905.

stantly descending charges of ore, reduces the ferric oxide to spongy metal, the change being accompanied by a slight evolution of heat:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2 + 8{,}652 \text{ cal.}$$

The zone in which this reduction occurs most rapidly is near the top of the furnace, its exact position depending on the nature of the ore, and its temperature varies from 600–900°. When the ores are porous they are more easily permeated by the carbon monoxide, and the reduction takes place more quickly than when denser ores are employed. The reduction in this upper zone is never quite complete, because metallic iron is itself oxidised when heated either in carbon dioxide or in carbon monoxide, free carbon being deposited in the latter case. As the spongy iron, still containing a small amount of oxide, descends it arrives at the hotter parts of the furnace, the temperature of which reaches 1000° in the belly or widest section. At this point the reduction of the metal is completed by the solid carbon present, some of which is supplied by the dissociation of carbon monoxide, which takes place at a high temperature, with formation of carbon dioxide and free carbon.[1]

Below this zone is the hottest part of the furnace, and the materials, which were formerly in a pasty state, melt completely, running down into the hearth, where the lighter slag floats on the surface of the heavier iron, and thus protects it from the oxidising action of the blast. Other important changes in the composition of the iron occurs as the metal passes down the furnace. In the first place, the spongy iron, in passing through the zone of reduction, takes up sulphur from the ores and fuel; and secondly, when the temperature reaches the highest point in the zone of carburisation, the phosphates contained in the ore are reduced, and the phosphorus is taken up by the iron. At a still higher temperature the fused iron in the presence of carbon reduces silicon from the silicates; and this, together with manganese and other metals, remains as a constituent of the cast iron.

It will thus be seen that three main zones may be distinguished in the furnace. In the *first* and highest, the greater part of the reduction occurs, whilst the partially reduced mass in passing through the *second*, acquires the high temperature

[1] Cailletet, *Compt. rend.*, 1866, **62**, 891.

which is necessary for the reactions occurring in the *third* and last zone. These comprise the complete reduction of the ore, the carburisation and fusion of the metal, and its impregnation with silicon, phosphorus, &c. These various zones are of course not well defined, but pass gradually one into the other.

541 *Gases of the Blast Furnace.*—The composition of the blast furnace gases naturally varies in the different zones and under different conditions of burden. The relation of the carbon dioxide to carbon monoxide present in the blast furnace gases is of great interest. The monoxide is reconverted during the reaction into the dioxide, and this either remains unaltered or is reconverted by the iron into the monoxide, according to the temperature which prevails in the upper part of the furnace. Carbon dioxide also is formed near the top of the furnace by the calcination of the limestone, and this is then partly reduced to the monoxide. The researches of Lowthian Bell and von Tunner have shown that the relation between the volumes of the escaping carbon dioxide and carbon monoxide, under otherwise similar conditions, serves as an excellent criterion of the economical working of the blast furnace, and the limit of economical working is reached when from 40 to 60 volumes of carbon dioxide are present for 100 volumes of carbon monoxide. The furnace gases contain, in addition, nitrogen of the air, hydrogen derived from the reduction of aqueous vapour, together with hydrocarbons, and frequently small traces of cyanogen or hydrogen cyanide.

Many analyses of the blast furnace gases, collected at various heights above the tuyères and under varying circumstances, have been made. The following figures give an idea of the varying nature of the composition of these gases:

Wood Charcoal Furnace at Veckerhagen, near Cassel. Height, 5·97 m. (Bunsen).

Depth in metres below the mouth—	0·86	2·59	4·32
Nitrogen . . .	62·34	63·89	64·58
Carbon dioxide . .	8·77	3·60	5·97
Carbon monoxide . .	24·20	29·27	26·51
Methane . . .	3·36	1·07	1·88
Hydrogen . . .	1·33	2·17	1·06
	100·00	100·00	100·00

Hot-blast Coke Furnace at Seraing in Belgium. Height, 14·43 m. (Ebelmen).

Depth in metres below the mouth—	0·30	3·05	13·71
Nitrogen	57·06	61·67	54·63
Carbon dioxide	11·39	1·08	—
Carbon monoxide	28·61	35·20	45·05
Methane	0·20	0·33	0·07
Hydrogen	2·74	1·72	0·25
	100·00	100·00	100·00

Cold-blast Coal Furnace at Alfreton. Height 11 m. (Bunsen and Playfair).

Depth in metres below the mouth—	1·52	5·18	10·36
Nitrogen	55·35	55·49	58·05
Carbon dioxide	7·77	12·43	—
Carbon monoxide	25·97	18·77	37·43
Methane	3·75	4·31	—
Hydrogen	6·73	7·62	3·18
Ethylene	0·43	1·38	—
Cyanogen	—	—	1·34
	100·00	100·00	100·00

When coal is employed in the blast furnace instead of coke, the waste gases are passed through coolers and scrubbers to remove the valuable tar and ammonia which they contain, and are then passed on to the Cowper stoves, &c.

Amongst the products of the blast furnace a variety of substances occur which choke or block up portions of the furnace. Thus in smelting zinciferous iron ores a compact incrustation of furnace-calamine, consisting chiefly of oxide of zinc, is found round the throat of the furnace, and no less than 100 tons of this compound, termed "gichtschwamm," are annually obtained from iron furnaces near Aix-la-Chapelle.

An interesting substance sometimes found in the blast furnace is a cyano-nitride of titanium (p. 819); and, in addition to this, "kish," or graphite, as well as silicates and the oxides of other metals, occur as solid deposits in the furnace.

Varieties of Cast Iron.

542 Fused cast iron usually contains 2·2–4·5 per cent. of carbon, and when the iron is cooled this is either entirely, or only partly, retained in combination by the metal, whilst the remainder separates out in the form of graphite, its behaviour being determined by the composition of the mass, the conditions of the process of manufacture, and the mode of cooling. When the greater part of the carbon separates in the form of graphite, the resulting metal is known as *grey iron*, whilst when the whole or the greater part of it is retained in combination by the iron, the metal is known as *white iron*. Between these are several intermediate conditions classed together as *mottled iron*. All these names are derived from the appearance of a freshly fractured surface of the metal, the mottling characteristic of the last class being caused by the occurrence of spots of grey in a matrix of white iron.

When white iron is dissolved in hydrochloric or sulphuric acid, various hydrocarbons are formed at the expense of the combined carbon which it contains, and these impart a peculiar and disagreeable odour to the hydrogen which is evolved. On the other hand, when grey iron is treated with acids the graphite separates out in the form of black insoluble scales. This fact was known to Bergman, whilst Guyton de Morveau proved that cast iron is formed when wrought iron is ignited with diamond powder; and Karsten showed that cast iron contains carbon both in the combined state and free in the form of graphite, this latter remaining behind when the iron is dissolved in an acid. The graphite can also be mechanically separated from the iron by sieving (Snelus).

Both the total amount of carbon present and the mode in which it occurs depend very largely on the other substances contained in the crude iron, whilst these of course are determined by the conditions of the manufacture. Thus chromium and manganese favour the presence of a large amount of carbon, which is retained in combination when the iron cools, whereas silicon and aluminium diminish both the total amount of carbon present and the proportion of it which remains in the combined form. The way in which the metal is cooled also has a very important influence on the mode of occurrence of the carbon, slow cooling promoting the crystallisation of graphite and the

consequent production of grey iron, whilst sudden cooling or chilling favours the production of the more homogeneous white iron. It is therefore possible, within certain limits, to obtain either grey or white iron from a given mass of the fused metal, simply by altering the conditions of cooling.

The following analyses of Cleveland pig[1] show the gradual variation in composition from grey through mottled to white iron :

	Grey.	Mottled.	White.
Carbon, Graphitic . .	3·20	1·84	—
„ Combined .	trace	1·25	3·05
Silicon	3·50	1·01	0·67
Sulphur	0·05	0·32	0·40
Phosphorus	1·67	1·57	1·60
Manganese	0·68	0·62	0·42

The properties of cast iron are also largely influenced by the amounts of silicon, phosphorus, sulphur, and manganese which are present.

White Iron is formed when the furnace is working on a heavy burden or at a comparatively low temperature. It is very hard and brittle, and when fractured presents a very close grain. It melts at a lower temperature than grey iron, is less liquid, and after cooling is often found to be vesicular or honey-combed from the evolution of gas given off as the metal cools.

Grey Iron, on the other hand, is produced at a higher temperature, has an opened grained fracture and melts to a thinner liquid, being thus better adapted for fine castings than white iron.

Mottled Iron is intermediate in its properties between white and grey iron.

Spiegel or *Specular Iron* is a variety of white iron in which manganese is present as an essential constituent, and contains a large proportion of carbon, varying from 3·5–6 per cent., practically all of which is in the combined form. It is extremely hard and brittle, and has a specific gravity of 7·6–7·7. When the alloy contains more than about 25 per cent. of manganese

[1] Quoted by Turner, *Metallurgy of Iron*, 3rd Ed., 280.

it attains a granular structure and is termed *ferromanganese.* These two varieties are largely used in the manufacture of steel by the Bessemer and open hearth processes.

A series of analyses of cast irons is given in the table on p. 1190.

Manufacture of Wrought or Malleable Iron.

543 Malleable iron can be produced, either by the direct reduction of the ore under such circumstances that it cannot take up sufficient carbon, &c., to convert it into cast iron, or indirectly from cast iron by the removal of carbon and some of the other constituents.

(I.) The Direct Reduction of Malleable Iron from the Ores.

544 *Iron furnaces.*—The simplest form of the iron furnace is that used at the present day on the west coast of India, as well as in the Deccan and Carnatic, and amongst the hill-tribes. The low-caste Hindoos who work in iron wander from place to place and build up their simple apparatus where they find fuel and ore ; this latter consisting generally of magnetic oxide or brown hæmatite. The furnaces are built on the ground and constructed in the form of a round shaft or chimney, from 2 to 4 feet in height, having a diameter at the bottom of from 10 to 15 inches, and at the top of from 6 to 12 inches. At the lower part there are two openings, one of which serves for the blast and the other for the exit of the slag which is formed by the silicates contained in the ore, as well as for the extraction of the bloom of iron. The bellows are usually made from a goat's skin or a buffalo hide, furnished with bamboo tubes. As soon as the furnace is warmed with charcoal, layers of the broken ore and charcoal are built in the shaft, and after from 4 to 6 hours a porous bloom of iron is obtained, varying in weight from 5 to 30 lbs., and this is then worked under the hammer. Throughout Central India and in the north-east provinces the manufacture of iron is somewhat further advanced, the furnaces being larger and of a similar character to those which have been or are still in use in various parts of the world, as in Africa, Borneo, and certain parts of Europe. In many localities in England furnaces were erected on high ground, so as to take advantage of the prevailing wind to increase the draught. The

Analyses of Cast Iron.

		Graphite.	Combined Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Chromium.	Iron.	Tungsten
White	Durham	—	4·10	0·23	0·03	0·07	2·37			
„	Alabama	0·10	2·92	0·95	0·30	0·64	0·10			
„	South Wales	—	2·40	0·80	0·70	1·50	0·20			
„	Staffordshire	0·20	2·00	0·71	0·19	0·47	0·50			
„	Schwechat	—	2·83	0·52	0·08	0·18	2·67			
Mottled	Ilsenburg	3·77	0·53	0·43	0·15	trace	1·43			
„	Cleveland	2·28	0·72	1·35	0·03	1·17	—			
„	Forest of Dean	2·37	1·31	0·40	0·06	0·07	0·11			
Grey	Forest of Dean	3·90	0·39	1·07	0·01	0·07	0·22			
„	Scotland	4·40	trace	2·68	0·08	0·10	—			
„	Staffordshire	3·30	0·40	1·88	0·02	0·71	0·40			
Spiegel	Dannemora	—	4·81	0·18	trace	0·12	1·99	—	92·90	
Spiegel	Siegen	—	5·04	0·41	0·08	—	5·75	—	88·56	
Ferromanganese	Prieger	—	7·15	0·87	0·02	0·07	72·75	—	19·14	
Ferrosilicon	Darwen	1·20	0·23	14·00	0·08	0·08	1·95	—	—	
Ferrochrome	Darwen	—	10·05	0·40	—	—	0·42	63·10	25·38	
Ferrotungsten	—	—	2·87	0·85	0·10	0·05	0·47	—	43·20	51·74

word "hammer," which frequently occurs in place-names in the south of England, usually marks the location of one of these old smelting works with its accompanying forge. Even to the present day the direct reduction of malleable iron from the ores is carried on in some European localities, especially in the Pyrenees and in certain districts of Spain, where a peculiar forge, termed the *Catalan forge*, is employed. The hearth of this furnace is about 3 feet long, 2 feet wide, and about 3 feet deep; at one side is an opening through which a tuyère is placed. The blast is supplied by the air carried down by a jet of falling water in a blowing machine termed a *trompe*. According to the size of the hearth the quantity of ore employed varies from 3 to 10 cwt., and this requires about its own weight, or rather more, of charcoal, and yields about 33 per cent. of iron. The ores employed are partly hæmatite and partly brown iron ore or spathic iron; the latter ores are previously roasted in order to expel water or carbon dioxide. At the beginning of the operation a weak blast is employed in order that the metal may be reduced by the carbon monoxide. The temperature is afterwards raised and pasty masses or blooms of metallic iron are obtained which need only to be brought under the hammer to yield marketable bar iron. By a similar process the Elba specular iron has been worked up in Corsica to within recent times. In the United States, especially in districts where charcoal is plentiful, similar *bloomery forges* are still worked with a hot blast of air. Some of these forges are capable of turning out a bloom of 300 pounds weight every three hours. The high bloomery furnace or "Stückofen" of the Germans is a blast furnace formerly in use in Carniola, and elsewhere, for the direct production of iron from the ore by reduction with charcoal. The process is, however, an expensive one owing to the large quantity of charcoal needed, and it has been superseded by other and cheaper methods.

(II.) Production of Malleable Iron from Cast Iron.

545 The change which occurs in the conversion of cast into malleable iron consists essentially in the removal of a large proportion of the carbon, silicon, sulphur, phosphorus, and manganese from the former, and is effected by oxidation in the presence of some substance which can unite and form a fusible slag with the silica and phosphoric oxide produced.

As the removal of carbon, &c., proceeds, the melting point of the iron rises, so that at a certain stage the metal begins to solidify. It is then worked into a porous ball or bloom, and hammered in order forcibly to squeeze out the slag which is contained in the pores.

In the older processes, the most important of which are the Styrian, Walloon, and South Wales processes, the oxidation is carried out in open-hearth furnaces, similar in general principle to that shown in Fig. 189. The cast iron is simply melted on

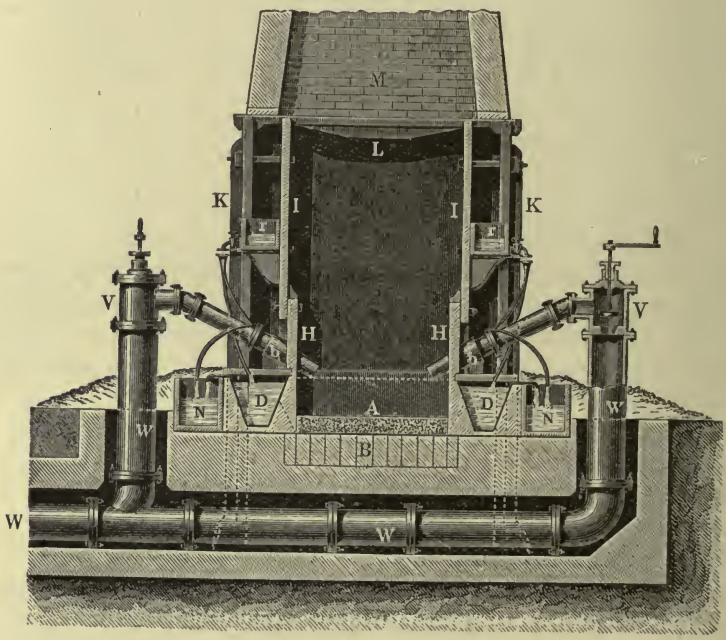


Fig. 189.

the hearth and exposed to a blast of air, by which it is partially oxidised. The oxides of iron thus produced react with the various constituents of the cast iron and convert them into their oxides, which either escape in the gaseous form (carbon) or unite with another portion of the oxide of iron to form a slag (silicon, phosphorus), whilst the oxide of manganese unites with a portion of the silica. This process is specially adapted for white iron, and when grey iron is used, the first melting (*refining*) simply converts it into white iron without greatly altering the total amount of carbon present, most of the silicon being at

the same time removed. A second similar operation (*fining*) is then necessary for the production of a satisfactory malleable iron.

The Puddling Process.—In 1784 Henry Cort introduced the puddling process, the essential feature of which is the use of a reverberatory furnace instead of an open-hearth furnace for the oxidation of the constituents of the cast iron. In the older form of the process the oxidation was effected chiefly by the oxygen of the air. The process was applicable only to white iron, and hence necessitated a preliminary *refining* of the metal when grey iron was employed. This was carried out in the furnace shown in vertical section and plan in Figs. 189 and 190. The metal was

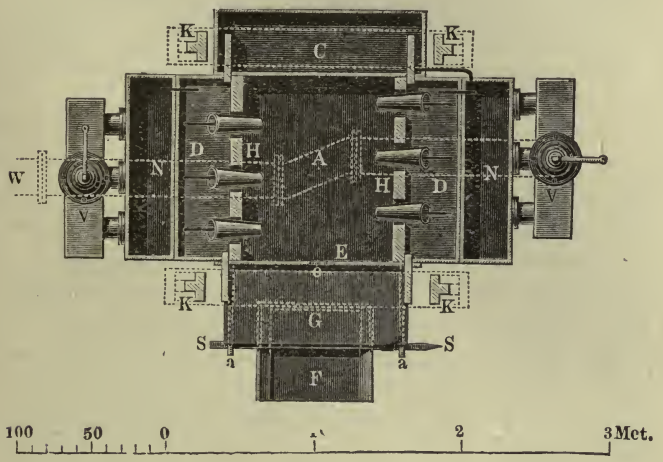


Fig. 190.

charged along with a sufficient quantity of coke on to the hearth A, and there melted and exposed to the blast from six tuyères. When the oxidation had proceeded far enough to reduce the percentage of silicon to the requisite point, the tap-hole was opened, the iron allowed to run into moulds, and the cast iron cooled by water. The refined iron is highly crystalline, white, and brittle, the carbon being present in the combined state. The following analyses by Abel of pig-iron, before and after refining, from Königshütte in Silesia, give the different percentages of silicon, phosphorus, and sulphur, and show that in this process the silicon is largely eliminated, whilst sulphur and phosphorus are less affected; the total amount of carbon, moreover, is not much altered.

	Pig-iron.	Refined iron.
Silicon	4·66	0·62
Phosphorus	0·56	0·52
Sulphur	0·04	0·03

The slag obtained in this process, known as *refinery-slag*, forms, when cold, a dark crystalline mass, with an almost metallic lustre. It consists chiefly of ferrous silicate, Fe_2SiO_4, in which, however, a part of the iron may be replaced by manganese, calcium, magnesium, &c. Not infrequently, distinct crystals of olivine, $(Mg,Fe)_2SiO_4$, have been found.

The refined iron was then melted on the bed of a reverberatory furnace and stirred by means of iron instruments, so as to expose it thoroughly to the air. As soon as the oxidation had been carried out to a sufficient extent, the metal was removed and treated as already described.

The Modern Puddling Process.—In England and other countries where grey pig is largely made, the preliminary process of refining has been done away with, and the pig-iron is at once submitted to the operation of puddling without previous refining, the process being termed "pig-boiling."

An ordinary puddling furnace is shown in elevation, section, and plan, in Figs. 191, 192, 193. The bed or hearth of the furnace (*h*) is supported by a cast iron plate; at each end of the hearth, which is usually 6 feet long, is a wall built of firebrick, one end being called the fire-bridge (*b*), and the other the flue-bridge (*d*). The bottom and side plates of the hearth are lined with a coating of tap-cinder, which is heated until it becomes soft, and is then spread evenly over the floor of the hearth. Above this is placed a coating or "fettling" of ferric oxide of about $1\frac{1}{2}$ inches in thickness, and this is renewed from time to time as it wears away. Neither of these coatings is shown in the figures. The fire-bars, which are sometimes placed in a slanting position, are seen at *r*, and the area of the grate should be from one-half to one-third of that of the bed. A powerful draught is obtained by means of a brick chimney, the top of which is furnished with a damper, which can be opened and shut at will by the workman by means of a handle, and thus the passage of air through the furnace regulated. In some furnaces gas is employed with a Siemens regenerator, and in America, petroleum, or even the gas from the petroleum springs, has been used as a source of heat.

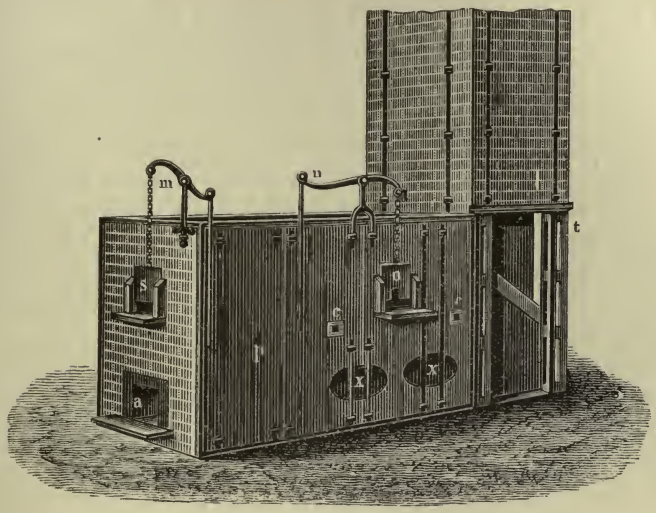


Fig. 191.

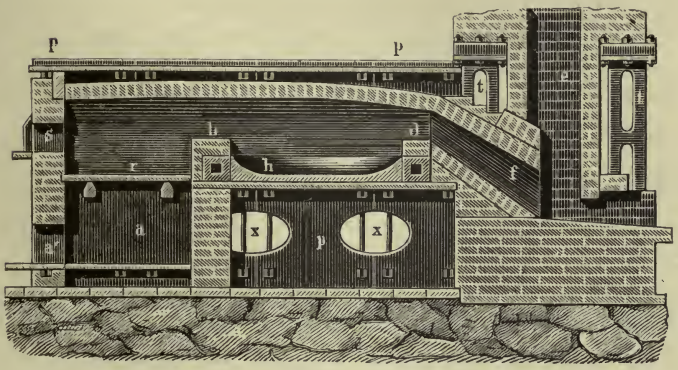


Fig. 192.

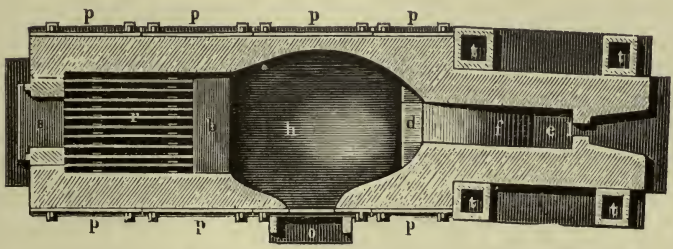


Fig. 193.

The distinguishing feature of the modern process consists in the fact that the iron is fused in contact with the oxides of

iron which are present in the fettling, and with a fusible slag which is added to each charge. In this way the oxidation of the carbon, &c., is carried out mainly at the expense of the oxygen of the fettling, and since an equivalent amount of metallic iron is thus produced the loss is rendered much smaller. In some cases, indeed, the malleable iron produced weighs more than the original pig. The time required for the oxidation is also greatly lessened, the whole operation lasting only two hours. As soon as the charge has been completely melted, it is well stirred, so that it is thoroughly exposed to the action of the fettling and of the air. It is then allowed to cool somewhat, and well mixed, whilst in a pasty state, with the oxide of iron present. This brings about the oxidation of the carbon with formation of carbon monoxide, probably according to the equation :

$$Fe_2O_3 + 3C = 2Fe + 3CO,$$

and the escape of this gas causes the whole mass to swell up or "boil." The iron then gradually subsides a little into a porous mass, or as it is termed, "comes to nature," and is worked into balls which are removed from the furnace and hammered to get rid of the fusible slag and to weld the porous iron into a homogeneous mass, this process being completed by passing the metal through the rolling mill. It is to this treatment that the characteristic fibrous structure of the wrought iron is due.

Mechanical Puddling Process.—In order to avoid the heavy manual labour necessary in the ordinary puddling processes, revolving puddling furnaces have been invented by Danks, Roe,[1] and others. These furnaces are in use to a small extent, but have not been generally adopted.

546 The following analyses made by J. G. Snelus give an idea of the consecutive chemical changes which take place in the passage from cast to wrought iron : (*a*) is the mottled Cleveland iron which was puddled in the Danks revolving furnace; (*b*) a portion taken out when melted; the composition ten minutes later is shown by (*c*); after a lapse of twenty minutes by analysis (*d*); the composition of the bloom is shown in (*e*); and of the puddled bar in (*f*); αC stands for combined carbon, and βC for graphite :

[1] *J. Iron Steel Inst.*, 1906, **71**, 264.

	Fe.	αC.	βC.	Si.	P.	S.	Mn.
a . .	93·19	1·45	1·38	1·24	1·49	0·11	0·63
b . .	95·03	2·83	—	0·82	0·91	0·09	—
c . .	96·46	2·80	—	0·20	0·58	—	—
d . .	98·09	1·17	—	0·05	0·52	—	—
e . .	98·40	0·15	—	0·09	0·45	—	—
f . .	97·13	0·15	—	0·14	0·47	0·04	0·14

It will thus be seen that the silicon is first burned out along with most of the manganese and phosphorus, whilst the carbon afterwards disappears.

Almost the whole of the phosphorus contained in the pig is found in the slag or *tap-cinder* as phosphide and phosphate; the sulphur is left in the cinder as iron sulphide. The tap-cinder is rich in iron, and is employed, after roasting in heaps, for the manufacture of a common kind of iron. The following analyses of tap-cinder give an idea of the composition of this material:

Analyses of Tap-Cinder.

SiO_2.	FeO.	MnO.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	P_2O_5.	S.	Analyst.
7·71	66·32	1·29	8·27	1·63	3·91	0·34	8·07	1·78	Riley.
11·76	58·67	0·57	17·00	2·84	2·88	0·29	4·27	3·11	,,
29·60	48·43	1·13	17·11	1·28	0·47	0·35	1·34	1·61	Percy.

547 *Properties of Malleable Iron.*—Good hammered and rolled bar-iron, when it contains from 0·1 to 0·25 per cent. of carbon possesses a fibrous texture, but when the amount rises to 0·5 or above it possesses a granular or crystalline structure. Fibrous iron is soft and possesses a grey colour; granular iron is harder and has a dead silvery lustre. The hardness of iron increases with the amount of carbon. Malleable iron melts at from 1,500° to 1,400°,[1] according to the amount of carbon which it contains. The physical properties of commercial malleable iron vary widely, being largely influenced by the nature and amount of the impurities which the iron contains; thus, for instance, sulphur imparts to iron the property of becoming brittle when hot, or, as it is technically termed, "red-short," whilst phosphorus renders iron weak at the ordinary temperature, when the iron is said to be "cold-short." Cold-short iron exhibits a peculiar fracture, and the property of cold-shortness apparently depends upon a peculiar crystalline condition of the iron.

Malleable iron of good quality should have a minimum

[1] Carpenter and Keeling, *J. Iron Steel Inst.*, 1904, **65**, 232.

tensile strength of 22 to 25 tons per square inch with the grain, and 18 to 20 tons per square inch across the grain; it should show an elongation of 18 to 25 per cent. on eight inches, and should bend nearly double without fracture.

(III.) The Manufacture of Steel.

548 Steel was obtained in early times directly from the ore in a similar manner to malleable iron.

Homer sings—

> And as when armourers temper in the ford,
> The keen-edged pole-axe, or the shining sword,
> The red-hot metal hisses in the lake;
> Thus in his eyeballs hissed the plunging stake.
>
> Pope's *Odyssey*, book ix.

These remarks evidently apply to steel, as wrought iron cannot be thus tempered. The Chalybes on the coast of the Black Sea were renowned for their ability in working the iron ores into steel, and the Greek name for steel, χάλυψ, appears to have been derived from the name of this tribe.

The older chemists looked upon steel as a peculiarly pure form of iron, and "Basil Valentine," in his *Last Testament*, terms it the "hardest, purest, most malleable iron." Lemery held peculiar views respecting steel. In his *Cours de Chymie*, published in 1675, he says: "Le fer est un métal fort poreux, composé de sel vitriolique, de soufre et de terre mal lié et digéré ensemble. On le réduit en acier par le moyen des cornes ou des ongles d'animaux, avec lesquelles on le stratifie et ensuite on le calcine; ces matières contenant beaucoup de sel volatile qui est alcali, tuent les acides de fer qui tenoient ses pores ouverts, et le rendent plus compacte."

Stahl considered iron to be an impure metal containing earthy materials, whilst steel was the pure metal saturated with phlogiston. Similar views were held by the later chemists. Bergman was the first to distinguish chemically between wrought iron, steel, and cast iron. He found that the first when dissolved in acids yielded the largest quantity of inflammable air, steel somewhat less, whilst cast iron gave the smallest quantity; hence he concluded that steel contained less phlogiston than wrought iron. He also showed that cast iron contained more graphite than steel, and this more than wrought iron, and hence he concluded that cast iron was converted into steel by loss of

graphite and by absorption of phlogiston, whilst he supposed that when steel was produced from wrought iron the opposite reactions occurred. Rinmann in 1782 developed similar views, and he especially insisted that malleable iron was a perfect metal, and was converted into steel by absorption of phlogiston, but that this phlogiston was not the substance usually thus designated, but plumbago. In 1786 Monge, Vandermonde, and Berthollet published a research proving that the difference between the various kinds of iron is determined mainly by the variation in the amount of carbon which they contain, but the many doubtful points which remained were cleared up only by the comprehensive researches of Karsten and Sefström.[1]

As already explained (p. 1172), the amount of carbon present has now been found not to provide a convenient distinction between malleable iron and steel, since specimens of these may contain the same amount of carbon and yet possess very different properties, owing to the difference in their internal structure.

Steel can be made in a very large number of different ways, the principles of which may be roughly summarised under the following heads:

A. Directly from the ore.
B. From malleable iron.
   1. By simple fusion.
   2. By the direct addition of carbon, accompanied or followed by fusion.
   3. By fusion accompanied by the addition of more highly carburised metal.
C. From cast iron.
   1. By the removal of carbon.
   2. By the addition of a less highly carburised metal, such as malleable iron.

Many of the processes actually adopted involve two or more of these methods, and the number of different processes now employed is very large, but only two or three of the most important and typical methods are here described.

549 *The Cementation Process.*—Sixty years ago the only method by which steel could be made was the decarburisation of the cast iron in the puddling furnace, and the subsequent

[1] Percy, *Iron and Steel*, p. 116.

re-carburisation of the puddled bar by the cementation process. The product was then either fused in a crucible, yielding cast steel, or drawn out under the hammer, whereby tilt steel or shear steel was obtained.

The cementation method of preparing cast steel is mentioned by Agricola in his *De Re Metallica*, whilst that for hammered or tilt steel was first described by Réaumur in 1722.

In the manufacture of steel by the cementation process carbon is added to the otherwise pure wrought iron. This is carried on in the furnace shown in Figs. 194 and 195. Into

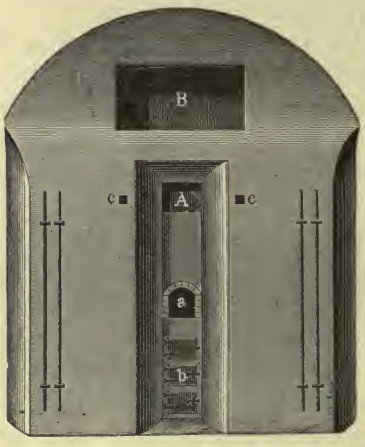


Fig. 194.

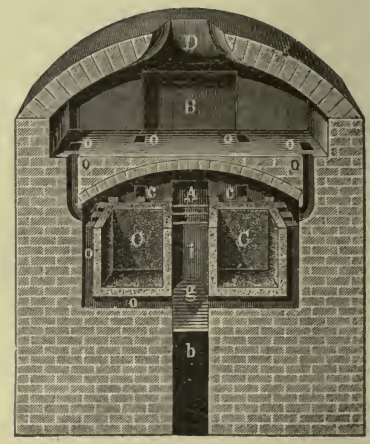


Fig. 195.

the furnace are built two square boxes or "converting pots," c c, Fig 195, of infusible fire-brick; and in these are placed the bars of iron which are to be converted into steel. The flames from a fire placed in the hearth (*g*) play round these boxes. The iron which has to be converted into steel is usually in the form of straight bars about 3 inches (75 mm.) broad, and 0·75 inch (18 mm.) thick, which are somewhat shorter than the converting pot in which they are placed. The interstices between the bars when piled in the pot are filled up with powdered charcoal, technically termed "cementing powder," a thick layer of the charcoal being placed on the top of the bars, and the whole mass plastered over with grinders' waste. The total weight of iron contained in each box is from five to six tons. The fire is gradually raised to a full red heat, or to about the melting point of copper, and is maintained

at this point for about seven to ten days, according to the quality of steel which is needed. Spring steel requires seven days, shear steel eight days, and steel for welding from nine to ten days. During the operation trial bars are removed by the openings (*c*) from the ends of the chests, and when it is found that the bar-iron has been completely converted into steel the furnace is allowed to cool, and after several days the charge is removed. The steel bars thus obtained retain the form of the original iron, but in physical properties they differ considerably from the original. Thus the coloured surface of the fractured bar of steel has no longer the bluish tint of malleable iron, but has acquired a reddish tint, not very different from that of bismuth, and the texture has become distinctly crystalline. The steel is also much more fusible than malleable iron, a varying amount of carbon having been taken up.

The following is an analysis by David Forbes of cementation steel made at Sheffield from Swedish iron :

Combined Carbon.	Graphitic Carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.
0·627	0·102	0·030	0·005	0·000	0·120.

An English cement-steel was found by Berthier to contain 1·87 per cent. of total carbon, and 0·10 per cent. of silicon, the remainder being iron.

A remarkable alteration of the surface is likewise noticed in the passage of wrought iron into steel, it being covered with blisters or blebs, and hence it is termed *blister steel.* The formation of these blisters is undoubtedly due to the production of gas within the bar, but the exact nature of this gas is somewhat doubtful. Probably it arises from the combination of a part of the carbon with oxygen derived from particles of oxide of iron contained in the interior of the bar. The bars are finally cut up, sorted according to their quality as indicated by the fracture, melted in plumbago crucibles, and finally cast in ingots.

Various hypotheses have been proposed to account for the phenomena observed in the cementation process. According to one view, the carbon is absorbed from the exterior and passes to the interior of the bar partly from the solid carbon, partly from the carbon monoxide formed by its partial combustion, and partly from the hydrocarbons derived from the hydrogen contained in the charcoal. The probability of the view that the

carbon monoxide is the active agent is strengthened by the fact observed by Graham, that red-hot iron has the power of absorbing from eight to ten times its volume of this gas. Others have assumed that the carburisation is brought about rather by the hydrocarbons than carbon monoxide, and that it is especially effected by the vapours of the potassium cyanide, formed by the action of potassium carbonate and carbon upon the nitrogen contained in the air still left in the boxes, and in support of this hypothesis it is stated that the cement powder loses its power after it has been used for some time and has lost its alkalis. It is also a well-known fact that the cyanides of the alkali metals have the power of giving up carbon to iron.

It also appears probable that the carburisation of the iron may be due in part, if not altogether, to an actual diffusion of the solid carbon into the bars, the blister steel being therefore a "solid solution" of carbon in iron. This phenomenon would then be analogous to the inter-diffusion of metals in the solid state which has been described by Roberts-Austen (p. 86).

550 *Crucible Steel.*—The cast steel made by melting cemented bars in a graphite crucible is of excellent quality, and is employed for the best classes of cutlery. Many other qualities of steel may also be obtained by the use of crucibles as already indicated; iron of various qualities being melted with carburising or decarburising materials, or with iron of a different carbon content.

One of these processes suggested by Karsten, but first carried out on the large scale by Krupp of Essen, consists in fusing pure wrought iron with the requisite quantity of spiegel. The progress which was made in the manufacture of cast steel by this process is illustrated by the fact that one of Krupp's cast steel six-pounder guns, weighing about 1000 kilos., exhibited in 1851, was considered a marvel, while in 1873 the same firm exhibited, in Vienna, a cast steel block weighing 52,500 kilograms, for the purpose of casting which 1,800 melting-pots, each holding thirty kilos. of steel, were employed.

In other cases malleable iron is melted with charcoal, or with cast iron; or again, cast iron is melted with iron ore. In all cases the molten metal cannot be immediately poured into the ingot mould, as the castings produced would then be full of vesicles. It is therefore allowed to remain in tranquil fusion for some time before pouring, or ferro-aluminium is

added, and the metal at once poured. The castings are then found to be sound and free from vesicles.

551 *Bessemer Steel Process.*—Since the year 1856 a complete revolution has taken place in the iron industry, and this has been caused mainly by the discovery of a method for manufacturing cast steel, on the large scale, from cast iron. This discovery was made by Bessemer,[1] and first communicated in a paper read before the Mechanics Section of the British Association, at its Cheltenham meeting, in 1856, and entitled "The manufacture of malleable iron and steel without fuel." The process consists in removing the carbon, silicon, and manganese contained in cast iron by oxidising them by means of a blast of air blown through the molten metal, the heat evolved by the oxidation being sufficient to keep the whole in a liquid state until the cast iron is converted into steel, which is thus effected without the intermediate laborious and costly processes of puddling and cementation. The first experiments which were made were unsuccessful, for although by this process the carbon and silicon can be removed, the phosphorus and sulphur which are contained in the pig remain in the finished steel, and for this reason the ordinary impure English cast iron yielded unsatisfactory results. The case, however, was otherwise when the pure Swedish charcoal-pig was used; indeed, the first real success in working the process was achieved with this iron at the Högbo Ironworks, at Sanviken, and this was followed by the successful use of grey iron made from the Ulverston hæmatite, and now technically known as *Bessemer-pig*. Other difficulties then arose such as the too complete oxidation, when the whole of the carbon is burnt out, a mass of pasty wrought iron being produced instead of liquid steel. This was overcome by the important suggestion made by Mushet[2] of the addition of spiegel at the end of the operation in such quantity as is necessary for the conversion of the whole of the wrought iron into steel.

The oxidation is carried on in an egg-shaped vessel, termed the converter (Figs. 196–7), made of wrought iron plates bolted firmly together and lined with an infusible siliceous rock termed gannister, which is ground, moistened with water, and applied in the form of a paste to the interior. The lower portion is an interchangeable bottom, consisting of a shallow lower section of the vessel with tuyère-box or wind-box and tuyères, together

[1] Patent, Dec. 7, 1855. No. 2768. [2] Patent, Sept. 22, 1856.

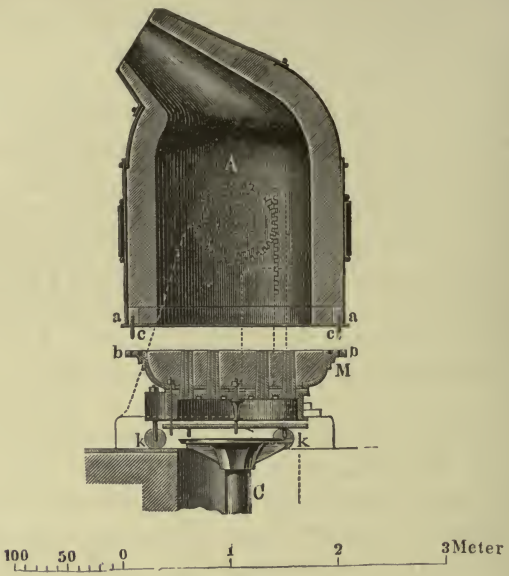


FIG. 196.

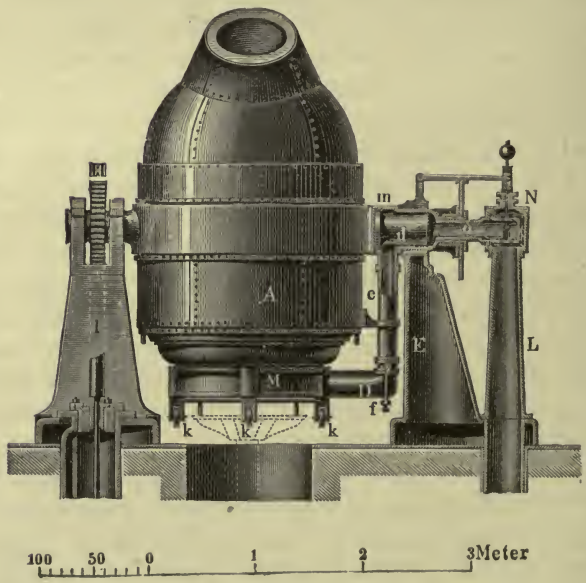


FIG. 197.

with the necessary arrangements for fixing these in their places. This bottom is attached to the vessel in such a manner that the

narrow space between it and the vessel lining may be rammed with plastic gannister by men working outside of the vessel, and this joint can be easily made at once upon pulling away the old bottom. This arrangement is of great advantage, inasmuch as by its use the number of blows per diem can be considerably increased. The pig-iron, which must be free from phosphorus and sulphur, is first melted in a cupola, and from five to twelve tons of this run into the converter, either directly from the cupola or from an intermediate ladle, the mouth of the converter being lowered to the proper angle to receive the molten metal. The converter is then gradually raised to the vertical position; at the same time a moderate blast of air is forced through the tuyères by means of the pipes L N and D, the pressure of the blast being afterwards raised to from eighteen to twenty pounds per square inch.

The combustion of the silicon, manganese, and carbon, as also of a portion of the iron, then begins, and the temperature rises to a point sufficiently high to keep the metal liquid. In the first part of the blow the graphite is converted into combined carbon, and a highly siliceous slag is formed, a portion of the silica being derived from the lining. When the first period is complete, an orange-yellow flame edged with blue appears at the mouth of the converter, and the second period, termed the "boil," then begins. In this, the slag containing oxide of iron oxidises the carbon, with formation of carbon monoxide which escapes throughout the mass, giving to it the appearance of a boiling liquid. During this period particles of the slag and molten iron are thrown out from the mouth of the converter, and a very brightly luminous flickering flame makes its appearance, accompanied by a rapid stream of sparks due to the combustion of the particles of iron. After the lapse of from six to eight minutes the intensity of the action diminishes, the shower of sparks ceases, and suddenly the flame disappears and is said to drop. The whole of the carbon has now been oxidised, and, if the blast be left on, the combustion is continued at the expense of a portion of the iron. Hence, the force of the blast is now lessened, the converter inclined, then the blast stopped, and the requisite amount of spiegel or ferromanganese introduced to bring the steel to the requisite degree of carburisation. The blast is then turned on again for a few seconds, or the mixture is simply allowed to stand for a short time, and the whole mass poured out into the ladle. After standing for a few minutes in the ladle the fluid

steel is cast into ingot moulds, and the cast steel worked up under the hammer and in the rolling mill. The whole process lasts from twenty to thirty minutes, and in this time from five to twelve tons of cast iron are converted into nearly the same weight of cast steel.

552 The chemical changes which the cast iron undergoes in the various stages of the Bessemer process, as well as the composition of the slags obtained, are exhibited in the following table:

(*a*) Composition of the pig-iron used (3,517 kilos.). (*b*) After the first period of twenty-eight minutes' blow. (*c*) After the second period of seven minutes' blow. (*d*) After the third period of three minutes' blow. (*e*) Finished steel (3,058 kilos.) after the addition of 168 kilos. of spiegel.

Composition of Bessemer Metal. No. 1.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	3·180	—	—	—	—
Combined carbon	0·750	2·465	0·909	0·087	0·234
Silicon	1·960	0·443	0·112	0·028	0·033
Phosphorus	0·040	0·040	0·045	0·045	0·044
Sulphur	0·018	trace	trace	trace	trace
Manganese	3·460	1·645	0·429	0·113	0·139
Copper	0·085	0·091	0·095	0·120	0·105
Iron	90·507	95·316	98·370	99·607	99·445

Composition of Bessemer Slag.

	a.	*b.*	*c.*	*d.*	*e.*
Silica	40·95	46·78	51·75	46·75	47·25
Alumina	8·70	4·65	2·98	2·80	3·45
Ferrous oxide	0·60	6·78	5·50	16·86	15·43
Manganous oxide	2·18	37·00	37·90	32·23	31·89
Lime	30·36	2·98	1·76	1·19	1·23
Magnesia	16·32	1·53	0·45	0·52	0·61
Potash	0·18	trace	trace	trace	trace
Soda	0·14	trace	trace	trace	trace
Sulphur	0·34	0·04	trace	trace	trace
Phosphorus	0·01	0·03	0·02	0·01	0·01

The following tables contain analyses of two other series of samples of Bessemer metal, taken at the end of each period of the process. As in the first Table, (*a*) represents the pig, and (*e*) the finished steel.

Composition of Bessemer Metal. No. 2.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	2·519	—	—	—	—
Combined carbon	1·000	3·040	1·640	0·190	0·370
Silicon	2·260	0·955	0·470	trace	trace
Phosphorus	0·073	0·070	0·070	0·070	0·059
Sulphur	0·107	0·091	0·098	0·093	0·090
Manganese	0·410	—	—	—	0·649

Composition of Bessemer Metal. No. 3.

	a.	*b.*	*c.*	*d.*	*e.*
Graphite	2·070	—	—	—	—
Combined carbon	1·200	2·170	1·550	0·097	0·566
Silicon	1·952	0·759	0·635	0·020	0·030
Phosphorus	0·048	0·051	0·064	0·067	0·055
Sulphur	0·014	trace	—	—	—
Manganese	0·086	—	—	—	—
Copper	—	—	—	—	0·039

Analyses No. 2 were made by Baker, at the Atlas Works, Sheffield, and analyses No. 3, by Snelus, at Dowlais.

Converter Gases.—Snelus has investigated the composition of the gases issuing from the converter. When the charge lasted eighteen minutes he found the following results on analysis of the gases drawn out at the times after the commencement of the blow given in minutes in the first horizontal line:

	2.	4.	6.	10.	12.	14.
CO_2	10·71	8·59	8·20	3·58	2·30	1·3
O	0·92	—	—	—	—	—
CO	—	3·95	4·52	19·59	29·30	31·11
H	88·37	0·88	2·00	2·00	2·16	2·00
N		86·58	85·28	74·83	66·24	65·55

Elimination of Phosphorus.—It was at first supposed that the non-elimination of phosphorus in the Bessemer process was due to the high temperature, and that if the process could be conducted at a lower temperature, as in puddling, all the phosphorus would be found in the slag. Messrs. Thomas and Gilchrist[1] and Snelus have, however, proved that it is possible to eliminate phosphorus completely in the Bessemer process by using a basic lining of calcined dolomite for the converter instead of the usual siliceous one, phosphate of lime and magnesia being produced. This is known as the "basic" process, and is now largely in use in the case of phosphoric pig; it

[1] *J. Iron Steel Inst.*, 1879, 120.

constitutes one of the most important advances in metallurgy, since it renders possible the direct production of steel from ordinary pig-iron, such as Cleveland pig, which contains comparatively large quantities of phosphorus.

The process is carried out in the main like the ordinary Bessemer process, but differs from it in one or two points. A certain amount of lime is placed in the converter and heated by the combustion of a small quantity of coke before the molten pig is run in. The blow is then conducted in the ordinary way, but when the flame has dropped the blow is continued, and it is in this "after blow" that the phosphorus is chiefly removed. This is well shown in the following table, which gives the results of a "blow" by the basic process: (*a*) gives the composition of the Cleveland pig, (*b*) after five minutes' blow, (*c*) after ten minutes, (*d*) after fifteen minutes, (*e*) after eighteen minutes. As soon as the phosphorus has been removed, a point which is indicated by the appearance of the fracture of a small sample of the metal, the process is concluded in the usual way by the addition of spiegel or ferromanganese. The slag, which contains the whole of the phosphorus in the form of phosphate, is ground and sold as a valuable manure.

	a.	*b.*	*c.*	*d.*	*e.*
Carbon	3·50	3·55	2·35	0·07	trace
Silicon	1·15	0·50	0·09	trace	0·00
Manganese	0·71	0·56	0·27	0·12	trace
Phosphorus	1·57	1·60	1·43	1·22	0·08
Sulphur	0·16	0·14	0·13	0·12	0·10

Application of the Spectroscope to the Examination of the Bessemer Flame.—It has already been stated that the point at which the flame drops is that at which it is found by practice to be necessary to stop the blast, but it is not always easy to hit this point with accuracy; and if the blow be stopped a few seconds too soon, or carried on for a few seconds too long the quality of the resulting steel suffers. The application of the spectroscope to the determination of this point was made by Roscoe in 1863,[1] and has since been investigated by Watts, Lielegg, Snelus, Hartley,[2] and others. It appears from these experiments that the point of complete decarburisation can be most exactly and easily determined by the sudden disappear-

[1] *Proc. Manch. Phil. Soc.*, 1862–3, **3**, 57.
[2] *J. Iron Steel Inst.*, 1895, **48**, 95; also 1901, **60**, 197.

ance of certain absorption bands observed in the spectrum of the flame. These bands, however, are not due in themselves to carbon, but to the presence of the oxides of manganese (Watts), the disappearance of this metal from the molten steel being simultaneous with that of the carbon.

553 *Open-Hearth Processes.*—In these methods a reverberatory furnace is used, such as that shown in section in Fig. 198, which represents a 12-ton Siemens regenerative steel furnace. The furnace works on the regenerative system exactly as described on page 580; CC′ and DD′ are the chambers used for absorbing the waste heat of the furnace and for heating the gas and air; *k* is the hearth of the furnace, made of infusible siliceous material in the acid process and of dolomite in the basic process, the latter being used when the pig-iron contains phosphorus.

In the simple Siemens process a charge of pig-iron, together with scrap iron or steel when available, is put on the hearth of the furnace and melted. When the charge is fused, iron ore in the form of hæmatite is added from time to time. A violent reaction takes place on the addition of the ore, slag first being formed by the oxidation of the silicon present to silica, which combines with ferrous oxide from the ore.

After the silicon has been oxidised and removed, the metal "comes to the boil," the carbon present being oxidised by the basic ferrous slag, carbon monoxide being evolved and a certain amount of iron liberated. The end of the process is determined by the quality of steel required, and is tested by taking out a small sample and judging by the fracture obtained.

When the process is finished, the metal is tapped and a small amount of ferromanganese added to deoxidise and recarburise it.

Instead of charging the furnace with pig-iron, liquid metal[1] is sometimes used direct from the blast furnaces, as this considerably shortens the time necessary to work off a charge.

In the basic open-hearth process, employed for making steel from phosphoric pig-irons, a certain amount of lime and limestone is charged in with the pig, ore, and scrap, and further quantities are added during the working, in order to keep the slag basic, the final slag containing from 40 to 50 per cent. of lime.

[1] The use of fluid metal in the open-hearth furnace, Riley, *J. Iron Steel Inst.*, 1900, **57**, 22.

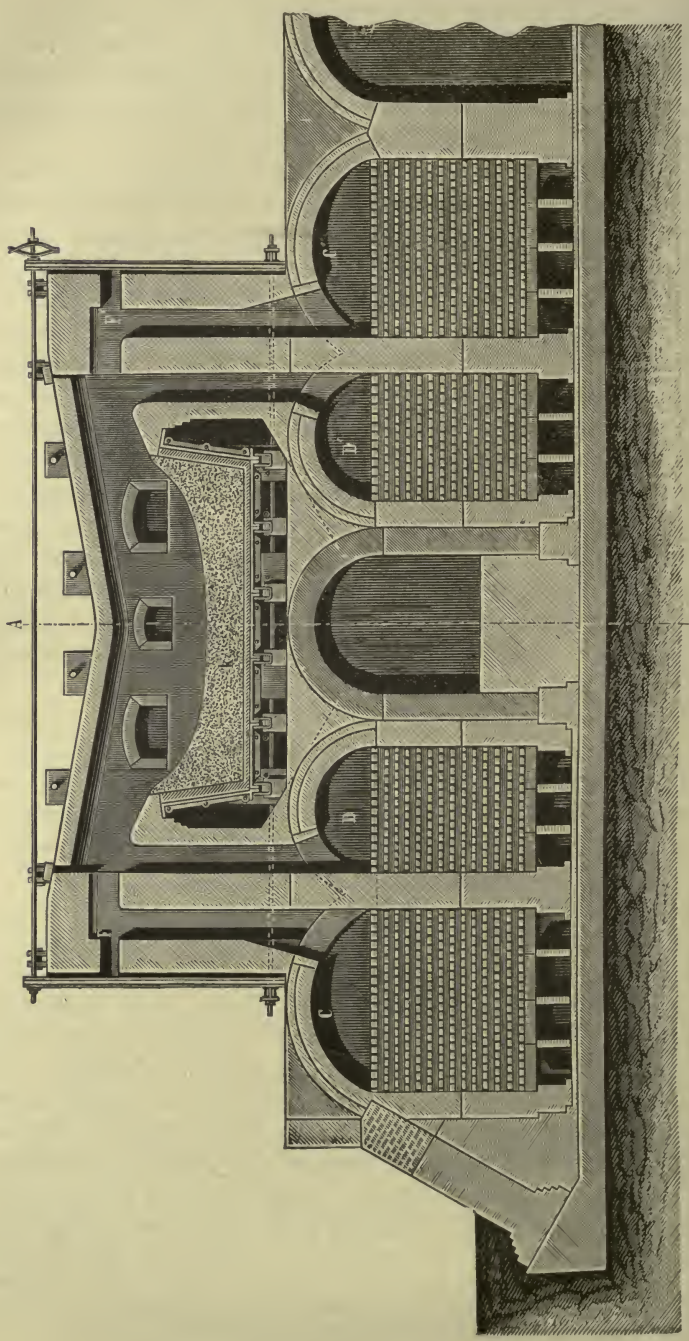


FIG. 198.

554 *Tilting Furnaces.*—Tilting furnaces[1] have been introduced to overcome the difficulties of tapping large charges from the furnaces. Of these the Wellman rolling-furnace is an example, in which the furnace is a strong steel shell lined with silica bricks. Underneath the body of the furnace are two curved rockers which roll on strong steel standards with horizontal surfaces. When pouring off slag or steel, the furnace is rocked forward by means of two hydraulic cylinders mounted on trunnions at their lower ends, and having the upper ends of their piston-rods attached to the pouring side.

Many modifications of the open-hearth process are now in use. Among these may be mentioned the Bertrand-Thiel[2] process, in which two or more furnaces are used to complete the operation. As generally practised, two open-hearth furnaces are used, preferably placed at different levels, so that the metal can easily be transferred from one to the other. Both furnaces are basic-lined. The pig is charged into the first furnace and is worked in the usual way; the scrap to be used is charged into the second furnace and is heated up and oxidised; the molten steel from the first furnace is then run into the second, where a vigorous reaction takes place, the non-metals being rapidly eliminated. By this process the time needed for working off a charge is considerably shortened and the yield materially increased, especially when large tilting furnaces and molten iron are used.

Another important modification is the Talbot process,[3] for which large basic-lined tilting furnaces are used, which have a capacity of 50 to 75 tons. The week's run is commenced on Sunday evening with a charge of pig and scrap, the charge being worked down to steel in the usual way with ore and lime. When this metal is of the required quality, about one-third of the charge is poured off, the furnace is turned back, and a considerable quantity of oxide of iron is added to the slag. When this is thoroughly melted, a charge of molten pig-iron is run in to replace the amount tapped out. A vigorous reaction at once takes place between the oxide of iron in the slag and the non-metals present in the iron, with a great elevation of temperature,

[1] Head, *J. Iron Steel Inst.*, 1899, **55**, 69.

[2] Bertrand, *J. Iron Steel Inst.* **51**, 1897, 115.

[3] The Open-Hearth Continuous Steel Process, Talbot, *J. Iron Steel Inst.*, 1900, **57**, 33.

so that during this reaction the gas-supply employed for heating the furnace is cut off. After the metal has "boiled" for ten or fifteen minutes, the slag is partly poured off and the bath finished off with additions of ore and lime. About one-third of the charge is again run off and the process is repeated as before, until the end of the week, when the furnace is emptied for repairs. The chief advantages claimed for this process are a saving in fuel, an increase in output and yield, and a saving in charges for labour and furnace repairs.

555 Electric furnaces[1] are being used to a considerable extent in the production of high-class carbon and special steels from cold scrap, and also in the refining of steel from open-hearth furnaces and Bessemer converters in order to improve its quality. Three types of furnace are used: (1) The Induction Furnace, (2) The Resistance and Arc Resistance Furnace, and (3) The Arc Furnace.

556 The ordinary Bessemer ingots are frequently found to be honeycombed and unsound from the presence of blowholes, and the same thing is found in all large steel castings. These blowholes are small cavities or bubbles distributed throughout the metal, and vary in size from visible holes to microscopic cavities. Many suggestions have been made for the prevention of blowholes, and one process largely used consists in exposing the molten steel during its solidification to enormous pressure by means of hydraulic machinery.[2] Casting under pressure was first attempted by Bessemer in 1856, but was reintroduced and rendered practicable by Whitworth in 1865.

For the production of sound castings and the elimination of blowholes, silicon and aluminium are often added to the molten steel, the silicon as ferro-silicon and the aluminium as metal; very little aluminium is required for the purpose, and in the finished steel generally only a trace can be found. The mode of action of these substances is not fully understood.

557 *Properties of Steel.*—The most characteristic property of high carbon steel is its power of assuming an almost adamantine hardness when quickly cooled, as when plunged into water. After this treatment it is extremely brittle, almost perfectly elastic, and so hard that it cannot be attacked by a file. The hardness and brittleness may be practically removed by annealing, that is to say, heating the steel to a high temperature and

[1] See Harbord's *Steel*, 4th ed., 1911, 261 *et seq.*

[2] Capron, *J. Iron Steel Inst.*, 1906, **69**, 28.

then allowing it to cool slowly. It may also be partially removed by a process of tempering which consists in heating the steel moderately and then allowing it to cool. The temper of steel depends upon the heat to which the steel is raised, and the workman judges as to the temperature by observing the various colours which the surface of the metal assumes during the progress of the operation. The tints thus observed are the colours of thin plates caused by the different thicknesses of the oxide formed on the surface. When the requisite tint is reached the object is quickly cooled by being plunged into water, brine, oil, &c. The hardest temper, such as is required for steel for surgical instruments, lancets, and razors, is that obtained at the lowest temperature; the tint employed for this purpose is that first reached, and is a light-straw colour, the temperature being about 230°. At 255° a brownish-yellow tint is attained, and steel thus tempered is best fitted for cold chisels and shears for cutting metals. At 265° the first shade of purple shows itself, and this is the temper employed for axes, plane-irons, and similar tools. A temperature of 277° gives a purple which is the tint for cutlery and cloth-shears, and for swords and watch-springs the metal is cooled when it has a bright blue colour, corresponding to a temperature of 288°. At higher temperatures, from 290° to 316°, steel assumes a dark-blue colour, and is used for shears, chisels, and especially for large saws.

The different degrees of heat may be obtained by dipping the several articles into a bath of carburised oil provided with a thermometer and heated up to the requisite temperature, although in ordinary cases this method is not carried out.

Damascening is produced by repeatedly welding, drawing out, and doubling up a bar composed of a mixture of steel and iron, the surface of which is afterwards treated with an acid. The surface of the iron retains its metallic lustre under the action of the acid, whilst that of the steel is left with a black, firmly attached coating of carbon.

Case hardening is effected by more highly carburising the surface of soft iron or steel. Objects of soft iron are heated together with nitrogenous organic matter such as powdered charcoal, bone-dust, leather, &c., or potassium ferrocyanide, and thus a superficial coating of more highly carburised steel is given to them.

The *Harvey process* is of a similar character, and is now applied to armour plates in order to give them a hard surface capable

of offering resistance to a modern projectile. This process is carried out by heating the plate of mild steel or nickel steel to about the melting point of cast iron in contact with carbonaceous material, which is tightly rammed down upon its surface. When the surface of the plate has absorbed about 1 per cent. of extra carbon the plate is withdrawn from the heating chamber and quenched with cold water.

The following tables give analyses (by Lambert) of various modern steels.

Manganese steel is very tough and is largely used for the jaws of rock breakers and other mining and mechanical machinery. Nickel is added to increase the tenacity and elastic limit, without reducing the ductility. Vanadium acts in a similar manner, but is much more efficient, 0·2 per cent. producing the same effect as 3 to 4 per cent. of nickel. Chromium increases the hardness, whilst tungsten and molybdenum prevent the softening effect of the rise of temperature of the tool.

	Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur	Copper.
Mild steel for structural work	0·247	0·476	0·063	0·052	0·049	0·054
Steel boiler plate	0·288	0·534	0·088	0·047	0·048	0·025
Steel rail, Indian Government	0·420	0·866	0·085	0·074	0·066	0·049
Steel tyre, N. B. Railway	0·534	0·902	0·248	0·045	0·054	0·038
Steel axle, British specification	0·320	0·756	0·186	0·038	0·035	0·051
Casting for hydraulic press	0·415	0·805	0·310	0·072	0·060	—
Casting for ship's stern frame	0·393	0·730	0·164	0·055	0·048	traces
Gun steel, British	0·385	0·648	0·182	0·038	0·035	0·029
Forged shaft for ship's propeller	0·345	0·555	0·096	0·040	0·042	0·055
Double shear steel	0·668	0·107	0·055	0·012	0·018	—
Spring steel, laminated, carriage	0·645	0·732	0·044	0·036	0·032	0·045
Tool steel for heavy work	0·750	0·468	0·238	0·021	0·018	0·022
Steel for swords, cutlasses, &c.	0·986	0·255	0·124	0·017	0·020	—
Die steel for striking coins	1·085	0·264	0·133	0·011	0·009	traces
Tool steel for light work	1·274	0·252	0·148	0·018	0·012	—
Cast steel for razors, surgical instruments, &c.	1·445	0·305	0·112	0·014	0·016	traces

	Carbon.	Manganese.	Silicon.	Phosphorus.	Sulphur.	Special Element.
Hadfield's manganese steel	0·875	13·330	0·068	0·030	0·047	—
Ordnance steel	0·330	0·606	0·165	0·029	0·038	Ni, 3·94
Chrome projectile steel	0·807	0·505	0·246	0·012	0·055	Cr, 5·74
Self-hardening tool steel	0·650	0·190	0·608	traces	0·042	W, 9·87
American self-hardening tool steel	0·585	traces	0·034	0·009	0·014	Mo, 9·18
Steel for motor-car work	0·250	0·378	0·135	0·058	0·024	V, 0·144

558 *Recalescence of Steel.*—When ordinary steels, containing varying amounts of carbon, are allowed to cool from a temperature of about 1000°, it is found that at two or more temperatures the regularity of the cooling is interrupted, an evolution of heat taking place which prolongs the period required for the metal to cool through a given range of temperature. This phenomenon is known as recalescence, and the temperatures at which the retardation during cooling takes place are indicated by Ar_1, Ar_2, and Ar_3; as these changes are reversible, there is an acceleration of the heating on raising the temperature of the steels, and the temperatures at which this acceleration takes place are indicated by Ac_1, Ac_2, and Ac_3. These changes do not generally take place at the same temperature, the Ac point often being 30° higher than the corresponding Ar point.

The Ar_3 change [1] is found only in steels containing not more than 0·38 per cent. of carbon, and varies from 900° in pure iron to 770° in a steel of this composition; the Ar_2 change takes place at about 770°; and the Ar_1 change takes place at about 700.° These changes are not equally well marked in all varieties of steel. The Ar_1 change is the most pronounced and can sometimes be observed when cooling down large masses; it can also be rendered evident by allowing a heated bar of steel to cool when loaded with a weight, just insufficient to bend it when hot. When the iron reaches the temperature of recalescence, it is seen suddenly to bend.

559 *Constitution of Steel.*—Two different views are held by chemists as to the constitution of steel, and the cause of hardening and of recalescence. Both agree in regarding the Ar_1 change as due to the formation of carbide of iron, Fe_3C. All carbon steels which are slowly cooled from above this temperature (700°) contain the greater portion of the carbon in the form of this carbide, whilst steel which is suddenly cooled from a higher temperature contains scarcely any of it.

According to one view (the "Allotropic"),[2] the two changes Ar_2 and Ar_3 mark the occurrence of allotropic changes in the iron present; the metal being supposed capable of existing in three allotropic forms, as γ-iron above Ar_3, as β-iron between Ar_3 and Ar_2, and as α-iron below Ar_2; of these varieties, γ- and β-irons are non-magnetic (see p. 1167). When heated steel is

[1] Carpenter and Keeling, *J. Iron Steel Inst.*, 1904, **65**, 224.

[2] See Stansfield, *J. Iron Steel Inst.*, 1899, **56**, 169; 1900, **58**, 317.

suddenly cooled, the γ- or β-form persists and the result is a hard and brittle metal; if the temperature be allowed to fall below Ar_2, the α-form is produced, and a soft metal is the result. In the absence of carbon, the β-form invariably passes into the α-condition, even when suddenly cooled, but carbon has a great tendency to retard this change, and thus, when present, keeps the iron in the hard form in quenched steels.

According to the second or "Carbon" view, the recalescence at Ar_3 marks the formation of an intensely hard sub-carbide of iron, $Fe_{24}C$, which remains unaltered if the metal is suddenly cooled. This carbide is easily decomposed by dilute acids with evolution of hydrocarbons, and it is actually found that when hardened steel is attacked by dilute acids, the greater part of the carbon is given off in this form. If the steel is cooled slowly, the carbide is decomposed at Ar_1 with evolution of heat into iron and carbide of iron, Fe_3C, and a soft metal is thus produced which leaves the greater part of its carbon behind in the form of Fe_3C when it is acted on by dilute acids. The change at Ar_2 is supposed to an alteration in the crystallisation of the iron.

The following are the most important constituents of steel:

Ferrite or pure iron occurs in trimorphic crystals with polygonal or rounded boundary lines produced by the interference of cubes or octahedra forming from a series of centres.

Pearlite.—A definite mixture of iron and carbide of iron Fe_3C, forming the eutectoid (p. 84). Pearlite contains 0·89 per cent. of carbon or 13 per cent. of Fe_3C; the carbon being molecularly associated with only about 12 per cent. of the iron, 87 per cent. of the latter being in the free state.

Hardenite.—According to Arnold this constituent also contains 0·89 per cent. of carbon, but in this case the carbon is associated with about 99 per cent. of the iron. It is found in quenched steels.

Austenite[1] is a solid solution of carbon in γ-iron, and is produced by quenching steels above the $Ar_{3\text{-}2\text{-}1}$ changes.

Martensite is a solid solution of carbon in β-iron, and is produced by quenching steels just below the Ar_3 change.

Troostite is a solid solution of carbon in α-iron, and is produced by quenching steels just below the Ar_2 change.

Sorbite is an emulsified form of pearlite in which the Fe_3C

[1] The constitution of iron-carbon alloys, *J. Iron Steel Inst.*, 1906, **72**, 493.

has not had time to segregate. It is formed by rapidly cooling the steel immediately after the Ar_1 change.

Sulphide of Iron is described by Arnold as occurring in masses or as a mesh-work in manganese-free steel and iron.

Sulphide of Manganese is very frequently present in steels as globules or cigar-shaped masses of a dull grey or dove colour.

Phosphide of Iron was observed by Stead[1] in 1900, and with free iron forms a eutectic similar to pearlite.

Manganese Silicate is very often present in steels, sometimes visible to the naked eye, sometimes only under the microscope.

Oxide of Iron is also often present in commercial steels.

Ghosts are drawn out segregations of ferrite, high in sulphur, phosphorus, and sometimes carbon, which appear dark when etched.

COMPOUNDS OF IRON.

Iron and Oxygen.

560 Iron forms three oxides,

Iron monoxide, or ferrous oxide, FeO,

Magnetic oxide of iron, or ferroso-ferric oxide, Fe_3O_4,

Iron sesquioxide, or ferric oxide, Fe_2O_3.

The last two oxides occur in nature as minerals, and are used not only as ores of iron, but also for medicinal purposes. Indeed, rust of iron (hydrated ferric oxide) is said to have been used as a medicine by Æsculapius, and Dioscorides also mentions *σκωρία σιδήρου*, (probably iron-scales), as being a substance similar to rust, but possessing less active medicinal properties. Red hæmatite was termed blood-stone, and the same author states that this may be obtained artificially by igniting loadstone. Pliny terms iron rust or scale *squama ferri*, red iron ore *hæmatites*, and loadstone *magnes*, and describes the action of the latter upon iron. The reddish-yellow and red oxide of iron is called *crocus martis* by the Latin Geber. The later chemists describe various methods for its preparation, and in 1735 the artificially prepared black oxide was termed *œtheops martis*. For a long time these compounds were distinguished only by their

[1] Iron and phosphorus, *J. Iron Steel Inst.*, 1900, **58**, 60.

different medicinal action. The supporters of the phlogistic theory considered them to be compounds of iron calx with various proportions of phlogiston. Thus, for instance, Scheele in 1777 states that the precipitate which an alkali produces in a solution of green vitriol when exposed to the air gives rise to crocus martis, and that fire-air or oxygen disappears. Hence he concludes that the precipitated calx gives up phlogiston in its conversion into crocus.

Lavoisier distinguished two oxides, æthiops and crocus. Other chemists, like Berthollet, believed that a large number of these oxides existed, and as late as 1811 the views of chemists on this subject were much divided. Gay-Lussac was the first to point out that in addition to the lower and higher oxide an intermediate compound exists, and this conclusion was confirmed by Berzelius.

Ferrous oxide acts as a basic oxide, yielding the readily oxidisable ferrous salts, FeR_2 (R = a univalent negative radical), in which the metal is divalent. Ferric oxide acts as a basic oxide, yielding the ferric salts, FeR_3, in which the metal is trivalent; it has also a feeble acidic function, forming with many basic oxides a series of compounds known as the ferrites, $M^{II}O,Fe_2O_3$. The magnetic oxide does not correspond to any characteristic series of salts, but yields a mixture of ferrous and ferric salts when it is treated with acids. It may be regarded as a ferrous ferrite, FeO,Fe_2O_3. Salts termed *ferrates* are also known corresponding to the acidic oxide FeO_3, which has not itself been prepared.

Iron Monoxide, or *Ferrous Oxide*, FeO, is obtained when hydrogen is passed over the sesquioxide heated to 300°, as a black powder which oxidises with incandescence on exposure, but loses this property after it has remained for twelve hours in an atmosphere of hydrogen (Siewert). The reduction of ferric oxide at a high temperature (700–1000°) by a mixture of hydrogen and steam yields a product which, although not pure, contains a high proportion of ferrous oxide.[1] This compound is formed also by the action of nitrous oxide on metallic iron at 200°.[2] When ferrous oxalate, FeC_2O_4, is heated at 150°–160° in absence of air, a mixture of monoxide and metallic iron remains, as shown by Liebig's observation that the gas evolved consists of fifty-six parts of carbon monoxide

[1] Hilpert and Beyer, *Ber.*, 1911, **44**, 1608.

[2] Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429.

and sixty-eight parts of carbon dioxide. If ferrous oxalate is added to boiling caustic potash the monoxide is obtained as a black velvety powder, which when washed with water in the air takes up oxygen (Böttger).

Ferrous Hydroxide, $Fe(OH)_2$, is formed when a pure ferrous salt is treated with caustic potash or soda freed from air. It is a white powder which, when washed with hot water and ether in absence of air, may be preserved in an atmosphere of hydrogen. As, however, it is difficult to obtain perfect absence of air, the ferrous hydroxide is usually obtained as a green pulverulent mass.[1] It crystallises from solution in strong caustic soda in flat green prisms.[2]

Ferrous hydroxide becomes heated on exposure to air, the mass sometimes becoming incandescent with formation of sesquioxide. It absorbs carbon dioxide rapidly, and dissolves in acids with evolution of heat. The moist hydroxide absorbs also atmospheric oxygen, assuming first a dirty-green colour, and finally undergoing conversion into the brown ferric hydroxide.

Ferrous hydroxide dissolves readily in acids to form the ferrous salts, which are produced also by the direct action of acids on metallic iron in the absence of oxidising agents, and by the reduction of the corresponding ferric salts. The anhydrous ferrous salts of colourless acids are usually colourless, but the corresponding hydrated salts possess a pale greenish-blue tint. The soluble salts possess a sweet, astringent, ink-like taste. Their neutral or acid solutions absorb oxygen slowly with formation of a ferric salt, part of which is precipitated in the form of basic salt when there is no excess of acid present. In presence of alkali, absorption of oxygen occurs rapidly, even at the ordinary temperature. In consequence of the ease with which they pass into a higher state of oxidation, the ferrous salts act as powerful reducing agents, and are largely employed for this purpose, both in the laboratory and in the workshop.

Magnetic Oxide of Iron, Ferroso-ferric Oxide, or Triferric Tetroxide, Fe_3O_4, occurs in large masses as the mineral magnetite. It crystallises in octahedra, dodecahedra, and other combinations of the regular system. It has an iron-black colour, and a more or less strong metallic lustre. It frequently

[1] Schmidt, *Annalen*, 1840, **36**, 101.
[2] de Schulten, *Compt rend.*, 1889, **109**, 266.

occurs in granular or amorphous masses, and is found also in marshes as an earthy mass known as ochreous iron ore (or in German *eisenmulm*). The pure crystallised mineral has a specific gravity of 5·18, whilst that of the granular and earthy material varies considerably, inasmuch as it contains magnesia, lime, and titanic oxide, and also often contains the iron in a more highly oxidised condition.

The interesting observation that this ore has the power of attracting iron, and that by contact with it iron attains the same polar magnetic properties, was made at an early date. According to some, the name is derived from a certain Magnes, who was the first to observe this property, whilst according to others the name is derived from Magnesia, a town in Lydia also called Heraclea, where the mineral was first found. The latter explanation would seem to be the more probable, inasmuch as Plato and Theophrastus termed magnetite the Heraclean stone. Ferroso-ferric oxide does not always possess the magnetic properties exhibited by loadstone, although attracted by the magnet.

When iron is heated to redness in the air it becomes coated with an iron scale. This is a mixture or a compound of the monoxide and sesquioxide in varying proportions. The inner layer, which is blackish-grey, porous, brittle, and attracted by the magnet, has the composition $6FeO,Fe_2O_3$, and is not magnetic. The outer layer contains a large quantity of ferric oxide, is of a reddish colour, and is more strongly attracted by the magnet than the inner portion. When iron is quickly burnt in oxygen or in the oxy-hydrogen blowpipe, the oxide which is formed varies in composition according to the conditions of the experiment, although it approaches the composition of the magnetic oxide; the occurrence of this oxide has also been observed in smelting operations.

Magnetic oxide is obtained when excess of steam or carbon dioxide is passed over red-hot iron, but, on the other hand, when the oxides of iron are heated in a current of hydrogen or of carbon monoxide in excess, they are reduced to metal. Pure ferroso-ferric oxide may be prepared by reducing ferric oxide at 400° by a mixture of hydrogen and steam.[1] When the black oxide is dissolved in hydrochloric acid, or when a mixture of a ferrous and ferric salt is dissolved in the right proportions, and caustic alkali added to the solution,

[1] Hilpert and Beyer, *Ber.*, 1911, **44**, 1608.

a black precipitate is obtained which dries to a brownish-black brittle mass giving a dark brown powder unalterable in the air. This hydroxide contains about 7 per cent. of water, and corresponds to the formula $Fe(OH)_2,Fe_2O_3$. It is attracted by the magnet, and may in this way be separated from any admixed sesquioxide.

Iron Sesquioxide, or *Ferric Oxide*, Fe_2O_3, is one of the most important ores of iron, occurring as red hæmatite, and as specular iron, crystallising in rhombohedra and scalenohedra, possessing a steel-grey colour. It also occurs under the name of micaceous iron in thin red translucent scales. This mineral is found in large quantity and in splendid crystals in the Island of Elba, of which Virgil [1] says: "Insula inexhaustis chalybdum generosa metallis." The crystals have a specific gravity of 5·19 to 5·25. The mineral martite is also a pure ferric oxide which crystallises in the same form as magnetic oxide, and is probably a pseudomorph of this mineral.

Ferric oxide can be prepared artificially in various ways. It is formed by igniting the hydroxide or any ferric salt containing a volatile acid, as a steel-grey crystalline powder, which, like all other kinds of iron sesquioxide, gives a brownish-red powder when finely triturated, and has a specific gravity of 5·17. It may be obtained in small crystals by the action of the vapour of ferric chloride on heated lime (Daubrée), or by fusing ferric oxide and borax together and treating the cooled mass with hot dilute hydrochloric acid; also by passing a slow steady stream of hydrogen chloride over the strongly ignited oxide (Deville). Artificial micaceous iron is prepared by heating a solution of ferrous sulphate and copper sulphate together for ten hours at a temperature of 210° (Wibel). Ferric oxide has also been observed in the crystalline state as a product in smelting operations, whilst crystals having the form of specular iron have been found in iron rust from a building some 700 to 800 years old. The ignited and natural ferric oxides dissolve only slowly in acids, the best solvent being a boiling mixture of eight parts of sulphuric acid and three parts of water. Ordinary ferric oxide is only very slightly paramagnetic and is not attracted by a small horse-shoe magnet. It has, however, been obtained in a more strongly magnetic form by the oxidation of ferrous hydroxide,[2] and Liversidge has described specimens of rust, which, although free from metallic iron and from ferrous

[1] Æn. x. 17–34. [2] Malaguti, *Compt. rend.*, 1862, **55**, 350.

oxide, are strongly magnetic. Heated in the electric furnace,[1] or in the oxy-hydrogen flame,[2] ferric oxide forms the magnetic oxide. The freezing point of ferric oxide, in an atmosphere of oxygen, is 1562–1565°.[3]

In addition to its use as an iron ore, ferric oxide is of service in a variety of other ways. Thus, the residue left in the process of distilling fuming sulphuric acid from green vitriol (Vol. I., p. 437), termed *colcothar* or *caput mortuum vitrioli*, is used largely as an oil-paint and also as a polishing powder; the least calcined portions, which are of a scarlet colour, are used as jewellers' rouge, whilst the more calcined portions, which have a bluish tint, are termed *crocus*, and are employed for polishing brass or steel. Noteworthy also is the employment of ferric oxide as catalyst in the contact process for the manufacture of sulphuric acid.[4]

Hydrates of Ferric Oxide.—A very large number of different hydrates of ferric oxide have been prepared, or exist naturally as minerals, but the exact constitution of many of these is uncertain. Brown hæmatite or limonite has the composition $2Fe_2O_3,3H_2O$, göthite Fe_2O_3,H_2O, and hydrohæmatite $2Fe_2O_3,H_2O$, all three being crystalline.

Muck[5] and Tommasi[6] obtained red hydrates by the precipitation of ferric salts with alkalis, and yellow hydrates by the oxidation of moist ferrous hydroxide or carbonate. By drying these at different temperatures Tommasi obtained various products which he regarded as definite hydrates, but van Bemmelen[7] has shown that all the "red" hydrates are in reality colloidal substances, the amount of water retained by them being dependent only on the pressure of the aqueous vapour in the atmosphere with which they are in equilibrium.

When freshly prepared red ferric hydroxide is heated with water under a pressure of about 5,000 atmospheres, it is converted into definite hydrates agreeing in composition with

[1] Moissan, *Compt. rend.*, 1892, **115**, 1034.

[2] Read, *Journ. Chem. Soc.*, 1894, **65**, 314.

[3] Kohlmeyer, *Metallurgie*, 1909, **6**, 323.

[4] Lunge and Pollitt, *Zeit. angew. Chem.*, 1902, **15**, 1105; Lunge and Reinhardt, *ibid.*, 1904, **17**, 1041; Keppeler and others, *ibid.*, 1908, **21**, 532, 577; *Zeit. physikal. Chem.*, 1908, **62**, 89.

[5] *Zeit. Chem.*, 1868, [2], **4**, 41.

[6] *Ber.*, 1879, **12**, 1929, 2334.

[7] *Rec. trav. chim.*, 1889, **7**, 37.

the naturally occurring minerals.[1] Between 30° and 42·5° limonite is formed, between 42·5° and 62·5° göthite, and above 62·5° hydrohæmatite. Under similar conditions the water content of the yellow hydrate obtained by the oxidation of ferrous hydroxide or carbonate scarcely alters between 40° and 70°, from which it would appear that this substance is not a true colloid.

Iron rust, when completely oxidised, is found to have a composition very close to that of limonite, viz. $2Fe_2O_3,3H_2O$; freshly formed rust, however, usually contains considerable quantities of ferrous hydroxide and carbonate.[2] Arsenious acid forms an adsorption compound with freshly precipitated ferric hydroxide[3]: the latter substance, therefore, can be employed as an antidote in cases of arsenical poisoning.

Ferric hydroxide dissolves readily in acids to form the ferric salts, which may be obtained also by the action of oxidising agents on the corresponding ferrous salts. In the anhydrous state they are generally colourless; in the hydrated state they are yellow or brown. The soluble ferric salts possess a peculiar astringent taste, and they pass readily by reduction into the corresponding ferrous compounds.

Soluble Ferric Hydroxide.—When freshly precipitated ferric hydroxide is added to a solution of ferric chloride it dissolves, forming a dark-red solution of basic ferric chloride, which may also be obtained by adding ammonium carbonate to a solution of ferric chloride until the precipitate first formed no longer redissolves. On dialysis of these solutions, hydrochloric acid and ferric chloride first pass through the membrane, and finally hydrochloric acid alone, leaving ferric hydroxide in solution in the dialyser (Graham). It is not possible, however, to remove all chlorine in this manner; thus after 210 days the composition of the residual solution was found to correspond to the formula $82Fe(OH)_3,FeCl_3$.[4] According to Tribot and Chrétien,[5] the last portions of chlorine may be removed by subjecting the liquid to electrolysis, the colloidal solution being placed in a porous cell containing the cathode, the outer cell containing water, which is frequently renewed.

[1] Ruff, *Ber.*, 1901, **34**, 3417. Compare Fischer, *Zeit. anorg. Chem.*, 1910, **66**, 37.

[2] Moody, *Journ. Chem. Soc.*, 1906, **89**, 720.

[3] Biltz, *Ber.*, 1904, **37**, 3138.

[4] Linder and Picton, *Journ. Chem. Soc.*, 1905, **87**, 1920.

[5] *Compt. rend.*, 1905, **140**, 144.

The solution usually gelatinises after a time, and this may be brought about rapidly by the addition of an electrolyte[1] or by electrolysis, when the gelatinous hydroxide separates at the cathode. Hydrochloric acid, nitric acid, sugar and alcohol do not bring about gelatinisation, but this is effected by traces of alkalis and of many acids. A similar solution may be obtained by the dialysis of the acetate, bromide, and other salts. This soluble hydroxide or hydroxychloride is used as a medicine under the name of *Liquor Ferri Dialysati.*

Soluble Meta-ferric Hydroxide, $Fe_2O_4H_2$.—This substance was discovered by Péan de St. Gilles.[2] It is formed when solutions of certain iron salts containing monobasic acids are heated for a length of time, and is precipitated from these solutions as a brown ochreous powder by the addition of a small trace of sulphuric acid. Meta-ferric hydroxide is insoluble in concentrated, but dissolves in dilute acids, forming solutions which exhibit the same optical properties as that of the hydroxide itself.

Ferric hydroxide forms a compound with sugar, which is soluble in water. This fact is of great importance to the sugar refiners, as this compound destroys the crystallising power of sugar, and therefore increases the quantity of molasses formed. Hence raw sugar ought not to be brought into contact with iron, and the "char" employed for the decolorisation of the sugar should be as free as possible from the compounds of this metal.

561 Ferric hydroxide has feebly acidic properties, and combines with strong bases to form unstable salts, termed *ferrites.* The compounds formed with the basic monoxides such as lime are analogous to ferrosoferric oxide, Fe_2O_3,FeO, which they resemble in being magnetic.

Alkali Ferrites.—Solutions of potassium and sodium ferrites are formed by boiling solutions of the corresponding ferrates, oxygen being evolved; the solution on standing deposits crystals of the ferrite, but these are very unstable and quickly decompose when removed from the alkaline liquid. A similar solution is obtained by boiling ferric hydroxide with concentrated caustic soda.[3] Sodium ferrite is produced also when ferric oxide is heated with sodium carbonate to bright redness, carbon dioxide

[1] See Freundlich, *Zeit. physikal. Chem.*, 1903, **44**, 131.

[2] *Ann. Chim. Phys.*, 1856, [3], **46**, 47. See also Scheurer-Kestner, *ibid.*, 1859, [3], **57**, 23; Debray, *Compt. rend.*, 1869, **68**, 913.

[3] Haber and Pick, *Zeit. Elektrochem.*, 1901, **7**, 215, 724.

being evolved. This reaction is made use of in the Löwig process for the manufacture of caustic soda from sodium carbonate (p. 317).

Calcium Ferrite, Fe_2O_3,CaO.—This compound is obtained when an intimate mixture of 190 parts of ferric oxide and 66·5 parts of lime is heated to whiteness in a platinum vessel for several hours.[1] It forms a brittle mass of interlaced acicular crystals exceeding an inch in length, with a dark metallic lustre and magnetic properties. When ground it yields a brown powder, which is obtained also by precipitating a solution of ferric chloride, as nearly neutral as possible, with lime water or saccharate of lime, and igniting the precipitate. Other calcium ferrites, containing different proportions of the two oxides, have also been prepared.[2]

Magnesium Ferrite, Fe_2O_3,MgO, occurs in nature crystallising in black octahedra as magnoferrite, and is obtained artificially by the ignition of a mixture of the two oxides in a current of hydrogen chloride, or by the precipitation of a mixture of ferric chloride and magnesium chloride with a quantity of caustic soda insufficient to throw down the whole. Many analogous compounds can be prepared in a similar way.[3]

Zinc Ferrite, Fe_2O_3,ZnO, was obtained by Ebelmen in black octahedra, by strongly igniting both oxides together with boron trioxide. The mineral franklinite has a similar composition.

562 *Ferric Acid*, H_2FeO_4.—This compound, like manganic acid, is not known in the free state. In the year 1702 Stahl noticed that when iron is fused with saltpetre and the solid mass lixiviated, or when a solution of iron in nitric acid is added to concentrated potash-ley, an amethyst or purple-red coloured solution is formed. Exactly a century afterwards Eckeberg published his memoir on "Yttria," in which he states that when gadolinite is fused with potash and the fused mass extracted with water, the solution possesses a dark purple-red colour, due to iron and not to manganese. The potassium ferrate formed under these circumstances was more carefully examined by Fremy.[4] It is prepared by igniting iron filings or iron oxide with saltpetre or caustic potash, or a mixture of both. The formation of the compound may be readily shown by heating a mixture of one part of powdered iron with two parts of saltpetre

[1] Percy, *Phil. Mag.*, 1873, [4], **45**, 455.
[2] Hilpert and Kohlmeyer, *Ber.*, 1909, **42**, 4581.
[3] List, *Ber.*, 1878, **11**, 1512. [4] *J. Pharm.*, 1841, **27**, 97.

in a small glass bulb, over a Bunsen burner. After a few minutes the mass becomes red-hot, and when cold the residue is dissolved in water.[1] The purple solution is obtained also by passing chlorine through a strong solution of caustic potash in which ferric hydroxide is suspended (Fremy).

Ferrates are readily produced also by the electrolytic oxidation of iron in caustic potash or soda solution. When iron is used as anode in concentrated caustic potash or soda solution and a low current density employed, all varieties of iron yield ferrate, but the yield is greatest with cast iron, smallest with wrought iron, and increases with the temperature. The best yield is obtained by immersing two large iron plates in concentrated alkali at 70° and making these alternately cathode and anode, the reversal taking place four times per minute. The iron plates become passive during the process.[2]

The concentrated potassium ferrate solution is almost black, and on addition of more potash deposits a reddish-brown precipitate, which is very unstable, but may be preserved by drying on a porous plate and sealing in a glass tube. As already mentioned, the solution decomposes on boiling, with evolution of oxygen and formation of a yellow solution of potassium ferrite, from which ferric hydroxide readily separates. Nitric acid and sulphuric acid yield a ferric salt with evolution of oxygen, whilst with hydrochloric acid chlorine is evolved.

Barium Ferrate, $BaFeO_4,H_2O$, is the most stable of the salts, and is obtained in the form of a dark-red powder by precipitating a solution of the potassium or sodium salt with barium chloride. It is fairly stable, and yields a red solution with acetic acid. It is not decomposed by dilute sulphuric acid in the cold, but at once yields ferric and barium salts with hydrochloric and nitric acids, with evolution of chlorine and oxygen respectively.[3]

Iron and Hydrogen.

563 Metallic iron absorbs from 0·5 to 1·0 volume of hydrogen when heated in the gas,[4] and in a similar manner hydrogen is occluded when dilute sulphuric acid is electrolysed with iron

[1] Hofmann, *Ber.*, 1869, **2**, 239.
[2] Haber and Pick, *Zeit. Elektrochem.*, 1901, **7**, 215, 712, 724.
[3] Baschieri, *Gazz.*, 1906, **36**, ii, 282.
[4] See Sieverts, *Zeit. physikal. Chem.*, 1911, **77**, 591.

electrodes. Electrolytically deposited iron always contains hydrogen when a high current density is used. The presence of hydrogen renders the iron harder and more brittle, but it is readily evolved on heating, the iron then resuming its original properties.

By the action of zinc ethyl, $Zn(C_2H_5)_2$, on anhydrous ferrous iodide in presence of ether, Wanklyn and Carius found that a mixture of ethylene, ethane, butane, and hydrogen is evolved, and that the residue on washing with ether yields a metallic powder resembling iron, which evolves hydrogen on heating and is decomposed by water with evolution of hydrogen, leaving a residue of metallic iron and ferrous oxide.[1] It appears probable that this product contains a definite compound of hydrogen and iron, but further investigation of the product is necessary to prove this supposition.

Iron and the Halogens.

564 *Ferrous Fluoride*, FeF_2, is obtained in colourless or greenish prisms, $FeF_2,8H_2O$, by dissolving iron in hydrofluoric acid and evaporating; these crystals decompose when gently heated, leaving the anhydrous salt; this is formed also when iron or ferric chloride is heated in dry hydrogen fluoride, and crystallises in colourless rhombic prisms.

Ferric Fluoride, FeF_3, is obtained by dissolving the hydroxide in hydrofluoric acid, colourless crystals of $2FeF_3,9H_2O$ separating out from the colourless solution on evaporation. The anhydrous salt may also be prepared in a similar way to the ferrous compound. It does not fuse even at 1000°, and forms ferric oxide when heated in the air.[2]

Several double salts with the alkali fluorides are known.

Ferroso-ferric Fluoride, $Fe_3F_8,10H_2O$, has been described.[3]

Ferrous Chloride, $FeCl_2$, is obtained by passing chlorine over iron filings (Thénard), but as a small quantity of ferric chloride is generally formed, even when an excess of iron is present, it is preferable to pass hydrogen chloride over iron filings or iron wire heated to redness (Wöhler and Liebig), or to reduce ferric chloride by heating it in a stream of pure hydrogen. Ferrous

[1] *Annalen*, 1861, **120**, 74.

[2] Poulenc, *Compt. rend.*, 1892, **115**, 941. Compare Recoura, *Compt. rend.*, 1912, **154**, 655.

[3] Deussen, *Monatsh.*, 1907, **28**, 163.

chloride is deposited in colourless shining scales, which, according to Sénarmont, are six-sided. It has a specific gravity of 2·528 (Filhol), and is very deliquescent, dissolving readily in water and alcohol. It fuses at a red heat, and volatilises at a yellow heat, when its vapour has a specific gravity of 6·38–6·67,[1] whilst at 1300–1500° it acquires the normal value of 4·3.[2]

When heated in the air it oxidises to ferric chloride, which volatilises, ferric oxide remaining behind:

$$12FeCl_2 + 3O_2 = 8FeCl_3 + 2Fe_2O_3.$$

When heated in a current of steam, magnetic oxide is formed:

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2.$$

When iron is dissolved in hydrochloric acid, and the solution concentrated in absence of air, bluish transparent monoclinic crystals of $FeCl_2,4H_2O$ are obtained; these have a specific gravity of 1·93, and deliquesce and become greenish coloured on exposure to the air, but effloresce at ordinary temperatures when kept over oil of vitriol. If a solution of this salt is evaporated with sal-ammoniac in absence of air, and the solid mass is heated in a flask until the whole of the sal-ammoniac is volatilised, the residue is anhydrous ferrous chloride. Hydrates with 1, 2, and 6 H_2O have also been obtained. Like other soluble ferrous salts, the solution of ferrous chloride absorbs nitric oxide, forming a dark, greenish-brown solution, possibly containing the unstable compound $FeCl_2,NO$ (p. 1242). The anhydrous chloride readily absorbs ammonia with evolution of heat and formation of a white powder (Faraday), which has the composition $FeCl_2,6NH_3$, gives off ammonia at 100°, and at higher temperatures yields ammonium chloride, iron nitride, and nitrogen.[3]

Ferroso-ferric Chloride, $Fe_3Cl_8,18H_2O$.—Magnetic oxide of iron dissolves readily in concentrated hydrochloric acid, forming a yellow liquid, which on concentration over sulphuric acid deposits the above salt in opaque yellow deliquescent crystalline crusts.

Ferric Chloride, $FeCl_3$.—The aqueous solution of this salt was known to Glauber under the name of *oleum martis*. He obtained it in the dry state by dissolving iron in hydrochloric

[1] Meyer, *Ber.*, 1884, **17**, 1335.

[2] Nilson and Pettersson, *Journ. Chem. Soc.*, 1888, **53**, 827.

[3] Fowler, *Journ. Chem. Soc.*, 1901, **79**, 288. Compare Girardet, *Bull. Soc. chim.*, 1910, **7**, 1028.

acid and evaporating the solution in a flask: "*In fundo* there remains a blood-red *massa*, which is as hot to the tongue as fire. It must be well-kept from the air, otherwise it liquefies to a yellow *oleum*."

Anhydrous ferric chloride is obtained by heating iron wire in a current of dry chlorine gas at a moderate red heat, when rapid combination with ignition takes place, ferric chloride being deposited. It is produced also when hydrogen chloride is passed over heated amorphous ferric oxide, and is not infrequently found in the craters of volcanoes.

Ferric chloride forms iron-black iridescent plates, or sometimes large hexagonal tablets, which exhibit a red colour by transmitted light, and a green metallic lustre by reflected light. It is very deliquescent, and easily soluble in water, alcohol, and ether. It volatilises readily even at 448°, and its vapour density at that temperature is less than is required by the formula Fe_2Cl_6. Hence its molecular formula is probably $FeCl_3$[1] (see p. 32). At higher temperatures it decomposes into ferrous chloride and chlorine. When dissolved in boiling alcohol or ether it appears to have a molecular weight corresponding to the formula $FeCl_3$.[2]

Ferric chloride forms with ammonia at the ordinary temperature the compound $FeCl_3,6NH_3$, which loses $2NH_3$ at 100°, and decomposes at higher temperatures, yielding ammonium chloride. It also absorbs nitrosyl chloride, yielding a dark-coloured deliquescent compound, $FeCl_3,NOCl$, and unites with nitric oxide at the ordinary temperature to form several unstable compounds, whilst at higher temperatures it is reduced by the gas to ferrous chloride.[3] When heated in a current of steam it is decomposed into ferric oxide and hydrogen chloride, and when heated in oxygen, chlorine is evolved, ferric oxide remaining. Anhydrous ferric chloride, intimately mixed with calcium and heated to dull redness, yields metallic iron.[4]

For the purpose of obtaining a solution of ferric chloride, the hydroxide may be dissolved in hydrochloric acid and the liquid evaporated in order to drive off excess of acid, or a solution of ferrous chloride may be heated with the requisite quantity of

[1] Grünewald and Meyer, *Ber.*, 1888, **21**, 687. Compare Friedel and Crafts, *Compt. rend.*, 1888, **107**, 301.

[2] Muller, *Compt. rend.*, 1894, **118**, 644.

[3] Besson, *Compt. rend.*, 1889, **108**, 1012; Thomas, *ibid.*, 1895, **120**, 447; **121**, 128.

[4] Hackspill, *Bull. Soc. chim.*, 1907, **1**, 895.

hydrochloric acid and the heated solution oxidised by addition of nitric acid. A solution of ferric chloride is, however, best prepared by dissolving iron wire in hydrochloric acid, as described under the preparation of ferrous chloride, and then passing chlorine into this solution until, after standing for some time, it smells strongly of the gas. The excess of chlorine is then displaced by passing a current of carbon dioxide through the warm liquid. A concentrated solution of ferric chloride has a dark-brown colour and an oily consistency. On dilution it becomes limpid, and has a slightly yellow colour.

Four different hydrates of ferric chloride have been described by Roozeboom:[1] $FeCl_3,6H_2O$, melting at 37°; $2FeCl_3,7H_2O$, melting at 32·5°; $2FeCl_3,5H_2O$, melting at 56°; and $FeCl_3,2H_2O$, melting at 73·5.° Solutions which contain more iron than corresponds to the formula $FeCl_3,2H_2O$ deposit the anhydrous salt when evaporated above the temperature of 66°. A deliquescent compound, $FeCl_3,HCl,2H_2O$, is formed by the action of hydrochloric acid on the pentahydrate, whilst similar compounds with $4H_2O$ and $6H_2O$ are also known.[2] The aqueous solution of the normal chloride is decomposed on heating, the more easily the more dilute the solution is, an insoluble oxychloride or soluble ferric hydroxide being produced according to the concentration of the liquid.[3]

The solutions of ferrous and ferric chlorides have long been used in medicine. An alcoholic solution of ferric chloride was formerly employed as a quack medicine of repute, known by the name of Lamotte's golden drops. This solution loses its colour when exposed to light,[4] ferrous chloride being formed, the latter compound separating, when the solution is not too dilute, in fine green crystals, $FeCl_2,2H_2O$.

Ferric chloride forms garnet-red crystalline double salts with the chlorides of the metals of the magnesium and alkali groups, such as $FeCl_3,MgCl_2,H_2O$; $FeCl_3,2KCl,H_2O$; and $FeCl_3,2NH_4Cl,H_2O$. These are decomposed by water, and a mixture of the last salt with an excess of sal-ammoniac is termed iron sal-ammoniac; it was formerly obtained by

[1] *Zeit. physikal. Chem.*, 1892, **10**, 477.

[2] Sabatier, *Bull. Soc. chim.*, 1881, [2], **36**, 197; Roozeboom and Schreinemakers, *Zeit. physikal Chem.*, 1894, **15**, 588.

[3] Compare Malfitano and Michel, *Compt. rend.*, 1907, **145**, 185, 1275; 1908, **146**, 338; 1908, **147**, 803; Michel, *ibid.*, 1908, **147**, 1052, 1288; Cameron and Robinson, *J. Physical Chem.*, 1907, **11**, 690.

[4] See Benrath, *J. pr. Chem.*, 1905, **72**, 220; 1909, **80**, 283.

sublimation of a mixture of iron oxide and ammonium chloride, and is mentioned by "Basil Valentine." Iron sal-ammoniac crystallises in yellow or bright-red transparent regular crystals from a dilute solution of ferric chloride; these contain a varying amount of iron, and rapidly absorb moisture from the air.

Iron Oxychlorides.—These compounds are formed in various ways. Some are soluble, whilst others are insoluble in water. When freshly precipitated ferric hydroxide is added to a solution of ferric chloride, it dissolves in considerable quantity, and a dark red liquid is obtained, which, to one molecule of chloride, may contain twenty or more molecules of oxide, and this on dialysis furnishes Graham's soluble oxide. These solutions may be diluted or warmed without any precipitation of ferric oxide. Many acids and salts, however, precipitate either ferric hydroxide or a basic chloride from these solutions, which latter is again soluble in water. If ferric chloride be incompletely precipitated with alkalis, a precipitate is obtained, which is soluble in water when it does not contain more oxide than is indicated by the formula $FeCl_3,5Fe(OH)_3$.

Insoluble basic ferric chlorides are formed, in the first place by the oxidation of ferrous chloride in the air; secondly, by roasting iron in the presence of hydrochloric acid or a chloride; and, thirdly, by boiling a solution of ferric chloride for some time. The composition and colour of these salts vary according to the mode of preparation. They are generally sparingly soluble in hydrochloric acid.

Ferrous Bromide, $FeBr_2$.—When bromine vapour is passed over iron heated to dull redness, heat is evolved, and a yellowish crystalline deposit of ferrous bromide is formed (Liebig). An aqueous solution of ferrous bromide can easily be obtained by dissolving iron in hydrobromic acid; on crystallising, bluish-green rhombic tablets are deposited, having the composition $FeBr_2,6H_2O$ (Löwig).

Ferric Bromide, $FeBr_3$.—This is obtained in the form of dark-red crystals by heating iron in an excess of bromine vapour. When heated in absence of air it fuses, and a part may be sublimed without decomposition, another portion, however, being decomposed into ferrous bromide and free bromine. The bromide deliquesces on exposure to air, and the solution, which may be simply obtained by dissolving the hydroxide in hydrobromic acid, decomposes on evaporation, with formation of insoluble

basic bromides. Like the chloride, the solution of the bromide dissolves ferric hydroxide readily with formation of soluble oxybromides. It forms double salts with certain of the alkali bromides.

An unstable ferric chlorobromide, $FeCl_2Br$, is formed by the direct union of ferrous chloride and bromine.[1]

Ferrous Iodide, FeI_2, is obtained by triturating iodine with a slight excess of iron filings, or by heating the latter in a covered porcelain crucible to redness, small quantities of iodine being gradually added; as soon as the whole mass becomes red-hot, a large quantity of iodine is thrown in, and the crucible is heated until iodine vapour ceases to be given off. On allowing the crucible to cool it is found that a further evolution of iodine vapour takes place, probably owing to the fact that the fused mass contains an unstable ferric iodide, which decomposes on cooling. The solid residue is a grey lamino-crystalline mass, which melts at 177°.[2] If a mixture of iodine and iron filings be warmed with water, these elements combine with evolution of heat, and a colourless aqueous solution of ferrous iodide is obtained, which on exposure to the air oxidises readily with separation of iodine. This decomposition is prevented by the addition of sugar. Ferrous iodide crystallises with $5H_2O$.

Ferric Iodide does not appear to exist.

Ferrous Perchlorate, $Fe(ClO_4)_2,6H_2O$, is the only iron salt of the oxy-acids of chlorine which is stable in the solid state. It is obtained by the double decomposition of ferrous sulphate and barium perchlorate (Serullas), or by dissolving iron in dilute perchloric acid (Roscoe). It forms pale-green deliquescent crystals, which give off water at 100°, and decompose at a higher temperature.

Iron and Sulphur.

565 *Iron Monosulphide*, or *Ferrous Sulphide*, FeS, occurs as troilite in small quantities in many meteorites, and is formed readily by the direct union of the elements. Iron wire burns in sulphur vapour with a bright light, and a roll of sulphur penetrates red-hot wrought iron and steel, but not cast iron, with formation of the molten sulphide.[3] In order to prepare this substance a mixture of three parts of iron filings and two

[1] Lenormand, *Compt. rend.*, 1893, **116**, 820.
[2] Wanklyn and Carius, *Annalen*, 1861, **120**, 69.
[3] Evain, *Ann. Chim. Phys.*, 1824, [2], **25**, 106.

parts of sulphur is thrown gradually into a red-hot crucible. The porous black mass obtained melts at a higher temperature, with separation of sulphur, if any higher sulphides have been formed, but as a rule the artificial sulphide contains an excess of iron, and this is removed by heating with excess of sulphur. For the preparation of the monosulphide, Berzelius recommends Gahn's process, namely, stirring a white-hot rod of iron in molten sulphur. The sulphide which is formed fuses and falls to the bottom of the crucible. The operation is continued as long as any free sulphur remains.

Pure monosulphide of iron is a yellowish crystalline mass, having a metallic lustre, and melting at 1300°.[1] It has a specific gravity of 4·89, is not magnetic, and does not lose sulphur when ignited in an atmosphere of hydrogen, or when raised to a white heat in absence of air. It is readily decomposed by hydrochloric and dilute sulphuric acids, forming sulphuretted hydrogen, and is used as a source of this gas in the laboratory. When heated in the air it oxidises, being converted partly into ferrous sulphate, whilst at a high temperature sulphur dioxide and ferric oxide are formed. Ammonium sulphide precipitates ferrous sulphide from solutions of ferrous salts as a black amorphous hydrated mass.

If seven parts of iron filings and four parts of sulphur are rubbed up to a paste with water a black sulphide is produced with evolution of heat. In this form it oxidises very quickly in the air with rise of temperature which, when the mixture is in large quantity, may lead to incandescence. Hence, according to Lemery, artificial volcanoes may be formed if several pounds of the above mixture be buried in the earth. The black amorphous sulphide is formed also by the reduction of ferric oxide or its salts in presence of sulphates and decomposing organic matter. This is the cause of the black deposit found in drains, as well as in the excrement, when iron is used as a medicine.

Iron Sesquisulphide, or *Ferric Sulphide*, Fe_2S_3, does not occur pure in the mineral kingdom, but probably forms a constituent of magnetic pyrites and copper pyrites. It is obtained by the action of ammonium sulphide solution on a solution of a ferric salt, so long as alkali is in excess,[2] but if the ferric salt be in ex-

[1] Treitschke and Tammann, *Zeit. anorg. chem.*, 1906, **49**, 320. Compare Allen, Crenshaw, Johnston, and Larsen, *Amer. J. Sci.*, 1912, **33**, 169.

[2] See Stokes, *J. Amer. Chem. Soc.*, 1907, **29**, 304: Malfatti, *Zeit. anal. Chem.*, 1908, **49**, 133.

cess a mixture of ferrous sulphide and sulphur is formed. It is produced also by the action of sulphuretted hydrogen on ferric hydroxide in presence of traces of ammonia, and is therefore the chief product formed in the purification of coal-gas from sulphuretted hydrogen (Vol. I., p. 871), as this gas always contains small quantities of ammonia.[1] In the dry way it is formed by gently heating sulphur and iron together, as well as by the action of sulphuretted hydrogen on ferric oxide at a temperature not above 100°. The sulphide obtained at a red heat forms a yellow non-magnetic mass which has a specific gravity of 4·4, and is decomposed by dilute hydrochloric acid into sulphuretted hydrogen, ferrous sulphate, and iron disulphide. Iron sesquisulphide forms compounds with the other sulphides.[2]

Potassium Ferric Sulphide, $K_2Fe_2S_4$, is obtained when iron filings, sulphur, and potassium carbonate are heated together, and the residue is extracted with water. The purple-coloured glistening needle-shaped crystals thus obtained have a specific gravity of 2·863, and burn when heated in the air, but when ignited in a current of hydrogen are converted without change of form into the black compound, $K_2Fe_2S_3$.

Sodium Ferric Sulphide, $Na_2Fe_2S_4,4H_2O$, is obtained in a similar way and forms brown microscopic needles. It is found in the "black ash" liquors obtained in the manufacture of soda by the Leblanc process (p. 297).

Silver Ferric Sulphide, $Ag_2Fe_2S_4$, is a dark brownish-black crystalline powder obtained by the action of silver nitrate solution on the potassium compound.

Cuprous Ferric Sulphide, Cu_2S,Fe_2S_3, occurs as the mineral copper pyrites.

Magnetic pyrites may be regarded as a compound of the mono- and sesqui-sulphides. Its composition varies between 5FeS, Fe_2S_3 and 6FeS,Fe_2S_3. It crystallises in hexagonal plates, usually, however, occurring in the massive state, having a brownish-yellow or brassy colour; it is attracted by the magnet, sometimes being itself magnetic. Its specific gravity varies from 4·4 to 4·7, and it frequently contains as much as 5·5 per cent. of nickel, the latter metal being obtained in Canada from this source in considerable quantities.

Iron Disulphide, FeS_2, occurs very widely distributed as iron

[1] Gedel, *J. für Gasbeleuchtung*, 1905, **48**, 400 : Stokes, *loc. cit.*

[2] Schneider, *Pogg. Ann.*, 1869, **136**, 460 ; Preis, *J. pr. Chem.*, 1869, **107**, 10 ; Malfatti, *Zeit. anal. chem.*, 1909, **48**, 352.

pyrites. This mineral was known in early times, but was not distinguished from copper pyrites, both being known under the name of πυρίτης. Agricola considered these as two varieties of the same mineral.

Iron pyrites is found in all geological formations ; it crystallises usually in cubes or pentagonal dodecahedra,[1] but occurs also in many other forms and combinations of the regular system, no fewer than sixty-nine different forms having been described. It is frequently found in spherical, botryoidal, or stalactitic masses, being formed by the action of organic matter on water which contains iron sulphate in solution. Hence it is frequently found in peat and coal in crystalline masses often possessing the form of the original organic matter, such as wood, roots, &c. It is likewise found in chalk cliffs, in similar concretionary forms.

In the pure state iron disulphide has a brass-yellow colour, and a specific gravity of 5·185. It is very hard, giving sparks when struck with steel, for which purpose it was formerly employed. Iron disulphide occurs also as radiated pyrites and marcasite forming bright brass-coloured rhombic crystals with a specific gravity of 4·68 to 4·85. This also is widely diffused, and occurs in various forms, especially in lignite beds. Iron disulphide may be obtained artificially by gently heating the monosulphide with sulphur, or by passing sulphuretted hydrogen over the oxides or chlorides of iron heated to redness. When an intimate mixture of ferric oxide, sulphur, and sal-ammoniac is heated slowly above the temperature at which the latter compound volatilises, the disulphide is obtained in small brass-yellow octahedra and cubes (Wöhler). Crystalline pyrites is formed also when carbon disulphide vapour acts upon heated ferric oxide (Schlagdenhauffen), and when ferric chloride is heated with phosphorus pentasulphide.[2] Iron pyrites and marcasite may be produced artificially also by the action of hydrogen sulphide on ferric sulphate solution.[3] Iron disulphide is not magnetic and is not attacked by dilute acids or sulphuric acid, but readily dissolves in nitric acid with separation of sulphur. There is some evidence showing that the iron in iron pyrites is in the ferrous condition.[4]

[1] See Pöschl, *Zeit. Kryst. Min.*, 1911, **48**, 572

[2] Glatzel, *Ber.*, 1890, **23**, 37.

[3] Allen, *J. Washington Acad. Sci.*, 1911, **1**, 170.

[4] Benedek, *Zeit. Kryst. Min.*, 1910, **48**, 447 ; Plummer, *J. Amer. Chem. Soc.*, 1911, **33**, 1487.

Iron Subsulphide, Fe_4S_3, is formed when iron is heated in the vapour of carbon disulphide, as a crystalline mass of specific gravity 6·957. It dissolves in dilute acids with evolution of hydrogen and sulphuretted hydrogen.[1]

Ferrous Sulphite, $FeSO_3$.—When iron is dissolved in aqueous sulphurous acid in absence of air, no gas is evolved, and the solution contains ferrous sulphite and ferrous thiosulphate:

$$2Fe + 3H_2SO_3 = FeSO_3 + FeS_2O_3 + 3H_2O.$$

The latter salt is a very soluble one; the first, however, is only slightly soluble, so that after a short time it is deposited in colourless or greenish crystals. When freshly precipitated ferric hydroxide is dissolved in sulphurous acid, a red solution is obtained, which quickly becomes decolorised with formation of ferrous sulphite, whilst, on the other hand, a solution of ferrous sulphite becomes red on exposure to the air.[2]

Ferrous Sulphate, or *Green Vitriol,* $FeSO_4,7H_2O$, was probably used by Geber. Agricola, in his discourse *De re Metallica,* mentions two kinds of pyrites. The one, such as coal-brasses, decomposes spontaneously and yields a vitriol; whilst the other, as the ordinary Mason's pyrites, does so only when it is roasted. Its preparation by dissolving iron in sulphuric acid was described by "Basil Valentine" in his *Treatise on Natural and Supernatural Things*: "Take oleum vitrioli; dissolve therein *mars,* and prepare a vitriol from it." In his last volume he describes the method for preparing sulphide of iron and for obtaining vitriol from it: "*Limaturam ferri* and *sulphur ana* calcined in a potter's furnace until it becomes tinted purple; then pour upon this distilled water, when a fine green liquid is formed. Draw this off *ad tertias,* allow it to deposit, and thus obtain an artificial vitriol." Green vitriol occurs as the mineral melanterite, either crystalline or in fibrous stalactitic forms, but generally massive and pulverulent. It is usually derived from the decomposition of pyrites or marcasite. Ferrous sulphate is likewise frequently found in solution in drainage water from mines, and it is manufactured on a large scale from this source. Large quantities of green vitriol (about 100 tons per week) are manufactured in South Lancashire from the pyrites occurring in the coal measures. These are piled up in heaps and exposed to the atmosphere. The soluble ferrous

[1] Gautier and Hallopeau, *Compt. rend.*, 1889, **108**, 806.

[2] See also Seubert and Elten, *Zeit. anorg. Chem.*, 1893, **4**, 44.

sulphate, together with the excess of sulphuric acid formed, runs into underground tanks, where the excess of acid is removed by means of scrap iron. On evaporating the liquor large crystals of ferrous sulphate are obtained. Ferrous sulphate is formed also as a by-product in the manufacture of copper sulphate or blue vitriol (p. 435). The commercial salt not infrequently contains traces of copper sulphate, and this may be detected and separated, as was pointed out by Vigani, so long ago as 1683, by leaving the solution in contact with metallic iron until the whole of the copper is precipitated. Another common impurity is ferric sulphate ; this may be removed by recrystallisation, but zinc sulphate, manganese sulphate, and other salts cannot thus be got rid of. Hence when chemically pure ferrous sulphate is needed it is best to treat an excess of iron wire with dilute sulphuric acid. When the evolution of hydrogen has ceased, the liquid is boiled together with the undissolved portion of the wire, filtered, and evaporated to crystallisation.

Ferrous sulphate forms well-defined monoclinic crystals with a specific gravity of 1·889 at 4° (Joule and Playfair), but is dimorphous, often crystallising in rhombic prisms, which are isomorphous with zinc sulphate. These are obtained when a crystal of zinc sulphate is thrown into a supersaturated solution of the ferrous salt, but, on the other hand, if a crystal of copper sulphate be employed, triclinic crystals having the composition $FeSO_4,5H_2O$ are obtained (Lecoq de Boisbaudran). When ferrous sulphate is heated in a vacuum to 140°, it yields a white powder of the monohydrate, $FeSO_4,H_2O$, and this, when gently heated in absence of air, yields the anhydrous salt, $FeSO_4$. Exposed to the air, the heptahydrate gradually loses water and becomes converted into basic ferric sulphate.

Up to 100° there are three hydrates which are successively in stable equilibrium with the aqueous solution, namely, the heptahydrate, stable from −1·82° (the eutectic point) to 56·6°, the tetrahydrate, from 56·6° to 64·4°, and the monohydrate, above the latter temperature.[1] The solubility at various temperatures, in grams of anhydrous ferrous sulphate per 100 grams of saturated solution, is as follows:

0°	10°	20°	40°	54°	64°	77°	90°
13·5	17·0	21·0	28·7	34·3	35·7	31·5	27·2.

[1] Fränckel, *Zeit. anorg. Chem.*, 1907, **55**, 223.

In addition to those already mentioned, hydrates with $6H_2O$, $3H_2O$, and $2H_2O$ have been described.

Ferrous sulphate is insoluble in concentrated sulphuric acid and absolute alcohol, and the addition of strong sulphuric acid to a saturated solution of the salt causes the precipitation of the monohydrate.[1] A solution of ferrous sulphate, like the chloride, absorbs nitric oxide. The dark brown saturated solution, which probably contains the compound $FeSO_4,NO$ (p. 1241), gives off the gas in a vacuum as well as when heated; in the latter case small quantities of nitrogen monoxide and ferric sulphate are formed. When the brown solution is mixed with strong sulphuric acid, care being taken to keep the mixture cool, it becomes of a purple-red colour: and upon this reaction the well-known test for nitric acid and the nitrates depends, as well as the method of detecting the presence of nitrous fumes in sulphuric acid.

Green vitriol is largely used in the arts and manufactures for the preparation of iron mordants, inks, Prussian blue, &c.

Ferrous sulphate enters into the composition of various double salts. There are, for instance, the red and yellow substances formed when sulphuric acid acts on a concentrated mixed solution of ferrous sulphate and copper sulphate.[2] Again, ferrous sulphate, like the sulphates of the metals of the magnesium group, copper, and manganese, forms crystalline double salts, with the sulphates of the alkali metals; of these the following is the most important.

Ferrous Ammonium Sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, is obtained when the calculated quantities of ammonium sulphate and green vitriol are dissolved in the minimum quantity of hot water, and the filtered solution is allowed to crystallise or is precipitated with alcohol. It forms clear, hard, bluish-green monoclinic crystals, which have a specific gravity of 1·813. One hundred parts of water dissolve (Tobler):

At	0°	20°	30°	60°	75°
$FeSO_4,(NH_4)_2SO_4$	12·2	21·6	28·1	44·6	56·7.

This salt is a very stable one, and does not readily undergo alteration in the air, being much less easily oxidised than green vitriol itself. Hence it is largely used instead of the latter salt for the purposes of volumetric analysis.

[1] Compare Kenrick, *J. Physical Chem.*, 1908, **12**, 693.

[2] Étard, *Compt. rend.*, 1878, **87**, 602; Scott, *Journ. Chem. Soc.*, 1897, **71**, 564; Allmand, *Zeit. anorg. Chem.*, 1909, **61**, 202.

Ferrous Disulphate, FeS_2O_7, separates out as a white powder when a concentrated solution of ferrous sulphate is mixed with several times its volume of concentrated sulphuric acid. It forms microscopic prisms, and is decomposed by water into sulphuric acid and green vitriol.[1]

Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by the action of nitric acid on a hot solution of green vitriol, to which the requisite quantity of sulphuric acid has been added:

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+2NO+4H_2O.$$

The yellowish-brown solution gives a syrupy liquid when concentrated, from which colourless crystals are deposited on standing. When these are heated, or when sulphuric acid is added to the concentrated solution, the anhydrous salt is formed as a white powder, which dissolves slowly in water, whilst by the action of green vitriol on boiling sulphuric acid the same salt is deposited in small crystalline scales or rhombic prisms:

$$2FeSO_4+2H_2SO_4=Fe_2(SO_4)_3+SO_2+2H_2O.$$

Various hydrates also have been described.[2]

When a dilute solution of ferric sulphate is boiled or incompletely precipitated with alkalis, or when a solution of green vitriol is allowed to oxidise in the air, various basic ferric sulphates are formed.[3] An iron mordant obtained by oxidising green vitriol with nitric acid deposits on standing large transparent crystals, which are probably monclinic, having the composition $FeSO_4(OH),7H_2O$; these are decomposed by water with formation of the insoluble salt, $Fe_2SO_4(OH)_4,5H_2O$.[4] Various other basic ferric sulphates occur as minerals,[5] being formed by the oxidation of the sulphides of iron. Amongst these may be mentioned vitriol ochre, $FeSO_4(OH)_4,2Fe(OH)_3,H_2O$. This frequently occurs in long brown, green, or ochreous yellow stalactites; whilst copiapite, $Fe_2(SO_4)_3,Fe_2(SO_4)_2(OH)_2,10H_2O$, occurs in sulphur-yellow tablets or crystalline scales, and fibro-ferrite, $2Fe_2(SO_4)_2(OH)_2,Fe_2SO_4(OH)_4,24H_2O$, forms a pale yellow or nearly white pearly or silky mass.

Anhydrous ferric sulphate, when heated, dissociates into ferric

[1] Bolas, *Journ. Chem. Soc.*, 1874, **27**, 212.

[2] Recoura, *Compt. rend.*, 1905, **141**, 108; 1907, **144**, 1427.

[3] Compare Cameron and Robinson, *J. Physical Chem.*, 1907, **11**, 641.

[4] *Ber.*, 1875, **8**, 771.

[5] See Scharizer, *Zeit. Kryst. Min.*, 1907, **43**, 113; 1909, **46**, 427.

oxide and sulphur trioxide. This fact is of importance in connection with the use of ferric oxide as a catalyst in the contact process for manufacturing sulphuric acid.[1]

Ferroso-ferric Sulphates.—The two sulphates of iron form various double salts, of which some are found in the mineral kingdom. Amongst these is roemerite, $Fe_3(SO_4)_4,12H_2O$, yellow monoclinic crystals, occurring at the Rammelsberg mine, near Goslar, together with another similar mineral termed voltaite, in which a part of the iron is replaced by isomorphous metals.

Ferric Potassium Sulphate or *Iron Alum*, $Fe_2(SO_4)_3,K_2SO_4,24H_2O$, is obtained when the proper quantity of potassium sulphate is added to a solution of ferric sulphate and the concentrated solution allowed to stand for some days about 0°. The salt forms bright-violet octahedra, and dissolves in about five parts of cold water. If caustic potash is added to the solution and the dark liquid allowed to evaporate, transparent yellowish-brown hexagonal crystals separate out which have the composition $5K_2SO_4,2Fe_2(SO_4)_2(OH)_2,16H_2O$, and possess the peculiar optical properties of tourmaline. This salt easily decomposes into iron alum and an insoluble basic ferric salt.

Ferric Ammonium Alum, $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, closely resembles the potassium derivative, and is sometimes termed "iron alum." Several other double salts of ferric and ammonium sulphates have been described.[2]

Iron and the Elements of the Nitrogen Group.

566 *Iron Nitrides.*—When nitrogen is passed over heated iron, the metal is rendered brittle, probably owing to the alternate formation and decomposition of an iron nitride, but the latter compound cannot be prepared in this manner. The nitride may, however, be obtained by heating the metal in ammonia, an observation first made by Berthelot, and confirmed by Stahlschmidt.[3]

If ammonia in excess is allowed to act on anhydrous ferrous chloride or bromide, or on finely divided reduced iron, or on

[1] Keppeler and D'Ans, *Zeit. physikal. Chem.*, 1908, **62**, 89; Wöhler, Plüddemann, and Wöhler, *Ber.*, 1908, **41**, 703; *Zeit. physikal. Chem.*, 1908, **62**, 641; Bodenstein and Suzuki, *Zeit. Elektrochem.*, 1910, **16**, 912.

[2] Lachoud and Lepierre, *Compt. rend.*, 1892, **114**, 915.

[3] *Pogg. Ann.*, 1865, **125**, 37.

iron amalgam at a temperature of about 420°, iron nitride is obtained as a dull grey powder.[1] In the compact state it is best obtained by heating iron wire or rod to a bright red heat with a large excess of ammonia, excess being necessary inasmuch as the hydrogen formed reduces iron nitride at the same temperature as that at which it is produced.[2]

The substance has a composition corresponding with the empirical formula Fe_2N, and is so brittle that it may be readily powdered in a mortar; it is somewhat magnetic, and has a specific gravity of 6·0–6·5. It readily oxidises when heated in the air, and ignites when warmed in chlorine. It is dissolved by dilute hydrochloric and sulphuric acids with evolution of hydrogen, and formation of ferrous and ammonium salts.

According to Guntz,[3] *ferrous nitride*, Fe_3N_2, and *ferric nitride*, FeN, both of which are black powders and differ from the foregoing, are formed by heating lithium nitride with ferrous potassium chloride and ferric potassium chloride respectively. A nitride of the formula Fe_5N_2 was found by Silvestri[4] as a lustrous metallic deposit on the Etna lavas. This is, however, possibly a mixture or solid solution of iron and the nitride, Fe_2N.

Ferrous Nitrate, $Fe(NO_3)_2,6H_2O$, is best obtained by the decomposition of green vitriol with barium nitrate, the filtrate being evaporated in a vacuum over sulphuric acid. It is very soluble in water and very unstable, easily passing into ferric nitrate. When iron is dissolved in cold dilute nitric acid, the following reaction takes place (Berzelius):

$$8Fe+20HNO_3=8Fe(NO_3)_2+2NH_4NO_3+6H_2O,$$

but the reaction varies greatly with the concentration of the acid and the temperature.[5]

Ferric Nitrate, $Fe(NO_3)_3$, is formed by dissolving iron in nitric acid. The brown concentrated solution deposits, on addition of nitric acid, according to the acidity and the concentration of the solution, colourless cubes of $Fe(NO_3)_3,6H_2O$, or colourless monoclinic crystals containing 9 molecules of

[1] Fowler, *Journ. Chem. Soc.*, 1901, **79**, 285; White and Kirschbraun, *J. Amer. Chem. Soc.*, 1906, **28**, 1343; Girardet, *Bull. Soc. chim.*, 1910, **7**, 1028.

[2] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1249.

[3] *Compt. rend.*, 1902, **135**, 738. [4] *Pogg. Ann.*, 1876, **157**, 165.

[5] Montemartini, *Journ. Chem. Soc.*, 1892, **62**, 1278.

water.[1] These are very deliquescent, and dissolve in water forming a brown liquid, which becomes colourless when concentrated nitric acid is added to it. Ferric nitrate is used as a mordant in dyeing and calico-printing.

Several soluble and several insoluble basic ferric nitrates are known.

Nitroso-compounds of Iron.—As already mentioned, nitric oxide is readily absorbed by solutions of ferrous salts with formation of dark olive-green to black solutions, which contain unstable compounds of nitric oxide with the ferrous salt. The maximum absorption for solutions of ferrous salts in water, alcohol, and other neutral solvents, is found to be in the proportion of 1 mol. NO to 1 mol. ferrous salt. The reaction, however, is reversible, the degree of dissociation not only varying with different ferrous salts, but being dependent also on the pressure, the temperature, the concentration of ferrous salt, the solvent, and the presence of other dissolved substances.[2] When dissolved in strong hydrochloric acid, ferrous chloride absorbs about twice as much nitric oxide as when dissolved in the same quantity of water.[3]

Anhydrous ferric chloride also absorbs nitric oxide, forming the compounds $2FeCl_3,NO$ and $4FeCl_3,NO$, which are reddish-brown non-crystalline hygroscopic powders. When nitric oxide is passed into an ethereal solution of ferric chloride, nitrosyl chloride is formed, and on evaporation over sulphuric acid, black needles of the composition $FeCl_2,NO,2H_2O$ are obtained, whilst at 60° the anhydrous compound $FeCl_2,NO$ is formed crystallising in yellow needles.[4]

In addition to the foregoing unstable nitroso-derivatives others of a more stable nature have been prepared. These were discovered by Roussin,[5] who prepared them by the action of ferrous sulphate on mixed solutions of the nitrites and sulphides of the alkalis, and they have since been investigated by many other chemists.[6] Their exact constitution has not yet been

[1] See Cameron and Robinson, *J. Physical Chem.*, 1909, **13**, 251.

[2] Manchot and Zechentmayer, *Annalen*, 1906, **350**, 368; Manchot and Hüttner, *ibid.*, 1910, **372**, 153.

[3] Kohlschütter and Kutscheroff, *Ber.*, 1907, **40**, 873.

[4] Thomas, *Compt. rend.*, 1895, **120**, 447.

[5] Roussin, *Compt. rend.*, 1858, **46**, 224.

[6] Porczinsky, *Annalen*, 1863, **125**, 302; Rosenberg, *Ber.*, 1879, **3**, 312; Pavel, *ibid.*, 1882, **15**, 2600; Marchlewski and Sachs, *Zeit. anorg. Chem.*, 1892, **2**, 175; Hofmann and Wiede, *ibid.*, 1895, **8**, 318; 1895, **9**, 295; 1896, **11**, 281; Marié and Marquis, *Compt. rend.*, 1896, **122**, 137.

determined, but they are closely allied to the ferrocyanides and similar compounds, and consist of salts of complex acids containing both the iron and nitroso-groups in the acid radical. Two classes of salts have been prepared, viz., the *ferrodinitroso*-derivatives, such as the salt $K[Fe(NO)_2S]$, and the *ferroheptanitroso*-derivatives, such as the salt $K[Fe_4(NO)_7S_3]$. The salts of the first named series have possibly a molecular formula double that given above.

Potassium Ferrodinitrososulphide, $K[Fe(NO)_2S],2H_2O$, is obtained by the action of potash on the heptanitrososulphide. It forms dark-red crystals, insoluble in water, and decomposes violently when heated, yielding, among other products, potassium and ammonium sulphates. By the action of sulphuric acid it yields the free *acid*, $H[Fe(NO)_2S]$, which slowly decomposes in the cold into sulphuretted hydrogen, nitrogen, nitrous oxide, and the heptanitroso-acid.

The corresponding salts of the other alkalis, and in addition the crystalline *ethyl* and *phenyl* derivatives, $C_2H_5[Fe(NO)_2S]$ and $C_6H_5[Fe(NO)_2S]$, are known. Potassium, ammonium, and sodium ferrodinitrosothiosulphates have also been prepared (Hofmann and Wiede).

Potassium Ferroheptanitrososulphide, $K[Fe_4(NO)_7S_3],H_2O$, is the most stable of these salts, and is obtained by adding a solution of ferrous sulphate to one of potassium nitrite and sulphide. It is formed also by boiling a solution of the ferrodinitrosothiosulphate, sulphur dioxide being evolved and ferric hydroxide precipitated. It forms dark monoclinic crystals with a diamond lustre, and is only sparingly soluble in water. Dilute sulphuric acid precipitates from its solution the free *ferroheptanitrososulphhydric acid* as an amorphous brown mass, but when the salt is heated with concentrated sulphuric acid it yields nitric oxide, nitrogen, sulphuretted hydrogen, sulphur, and ferric ammonium and potassium sulphates.

The corresponding alkali salts have been obtained and also the *thallium* salt. The *ammonium* salt is formed by the action of nitric oxide on freshly precipitated ferrous sulphide suspended in water, part of the nitric oxide being reduced to ammonia.[1]

567 *Phosphides of Iron.*—In the year 1780, J. C. F. Meyer,

[1] See also *Atti R. Accad. Lincei*, [5], 1906, **15**, ii., 467; 1907, **16**, i., 654; ii., 542, 584, 658, 740; 1908, **17**, i., 202, 424, 545; Rosenberg, *Arkiv Kem. Min. Geol.*, 1911, **4**, No. 3.

while examining the cause of the cold-shortness of iron, came to the conclusion that this was produced by the presence of a peculiar metal to which he gave the name *hydrosiderum*. The subject was investigated shortly afterwards by Bergman, who found that when the residue obtained by dissolving cold-short iron in sulphuric acid is fused before the blowpipe with reducing agents, a metallic bead is obtained which he also believed to be a peculiar metal; to this he gave the name of *siderum*. In 1784, Meyer repeated his experiments and came to the conclusion that the substance thus obtained was a compound of iron and phosphoric acid, and it was afterwards ascertained that the body formed by reduction on charcoal was a phosphide of iron.

One phosphide of iron, Fe_2P, is obtained as a porous non-magnetic powder by fusing ferrous or ferric phosphate with lamp-black under a layer of sodium chloride, and in lustrous grey crystals by fusing cuprous phosphide with 10 parts of iron filings in the electric furnace.[1] When heated in the air it is converted into a basic phosphate, $2Fe_2O_3,P_2O_5$.

The phosphide Fe_3P is obtained from fused mixtures of phosphorus and iron containing more than 84·4 per cent. of iron, and is prepared also by fusing copper phosphide with a sufficient quantity of iron, when the compound Fe_3P, in an almost pure state, rises to the top as a separate phase.[2] This phosphide dissolves in concentrated hydrochloric acid, giving ferrous chloride, phosphoric acid, and pure hydrogen.

When iron pyrites or iron powder is ignited in a stream of phosphine a grey non-magnetic powder, having the composition Fe_3P_4, is obtained, whilst the compound FeP is left as a dark-grey powder when the monosulphide is ignited in the same gas, or when iron is heated in phosphorus vapour. The compound Fe_2P_3 is produced by strongly heating phosphorus and ferric chloride placed in separate boats in a tube in a current of carbon dioxide, and forms hard metallic non-magnetic crystals.[3]

When obtained in distinct crystals these phosphides of iron are mostly insoluble in single acids, but dissolve in a mixture of nitric and hydrofluoric acids, whilst in the loose porous state they

[1] Maronneau, *Compt. rend.*, 1900, **130**, 656.

[2] Le Chatelier and Wologdine, *Compt. rend.*, 1909, **149**, 709. Compare Stead, *J. Iron Steel Inst.*, 1900, **58**, 60; Saklatwalla, *ibid.*, 1908, **77**, 92; Gercke, *Metallurgie*, 1908, **5**, 604; Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1220.

[3] Granger, *Compt. rend.*, 1896, **122**, 936.

are attacked by hot hydrochloric acid with evolution of phosphine and formation of phosphoric acid. They do not undergo alteration in the air, and can be fused in all proportions with metallic iron. Many other iron phosphides which have been described, and possibly some of the above, are probably in reality mixtures of a true phosphide and iron.[1]

Ferrous Phosphate, $Fe_3(PO_4)_2,8H_2O$, occurs as the mineral vivianite, crystallising in monoclinic prisms. In its pure state it is colourless, but it generally possesses a green or blue tint, owing to partial oxidation. It is found also as an earthy mass termed blue iron earth, sometimes dispersed through clay, and together with bog iron ore, and in the cavities in fossil bones. When a solution of green vitriol is precipitated with sodium phosphate, a white precipitate is obtained, which, however, soon becomes blue or green on exposure to air. If the liquid and the precipitate are allowed to stand together for a week at a temperature of 60–80°, the compound is converted into small crystals which become blue on exposure to the air (Debray). The precipitated phosphate is used in medicine.

When iron is dissolved in a solution of phosphoric acid, colourless needles, having the composition $Fe(H_2PO_4)_2,2H_2O$, are deposited after some time, and these alter rapidly on exposure to air.[2]

Ferric Phosphates.—The *normal orthophosphate,* $FePO_4,2H_2O$, is obtained as a yellowish-white precipitate by adding ordinary sodium phosphate to normal ferric chloride. It is soluble in dilute mineral acids, but not in cold acetic acid, and is slowly decomposed by water. When ferric hydroxide is dissolved in orthophosphoric acid and the solution rapidly evaporated, the *diacid salt,* $Fe(H_2PO_4)_3$, is obtained as a pink crystalline powder, which decomposes in moist air and deposits crystals of the *monacid salt,* $2FeH_3(PO_4)_2,5H_2O$ (Erlenmeyer). *Ferric metaphosphate,* $Fe(PO_3)_3$, is deposited in pink plates when ferric hydroxide is digested with glacial phosphoric acid at 100°.[3]

Basic iron phosphates occur in nature, and frequently form a constituent of limonite. Ferric phosphate also occurs as dufrenite, $Fe_2(OH)_3PO_4$, which is found sometimes in rhombic

[1] See Le Chatelier and Wologdine, *loc. cit.*; Kuhn, *Chem. Zeit.*, 1910, **34**, 45.

[2] Erlenmeyer, *Annalen*, 1878, **194**, 182.

[3] Hautefeuille and Margotte, *Compt. rend.*, 1888, **106**, 135. See also Johnsson, *Ber.*, 1889, **22**, 976.

crystals, but more generally in needles or as a radiated fibrous mass. Vivianite is often oxidised and is converted into beraunite, $Fe(PO_4),2Fe_2PO_4(OH)_3,4H_2O$, occurring in small foliated aggregates having a hyacinth-red colour.

568 *Arsenides of Iron.*—When metallic iron is ignited with an excess of arsenic in the absence of air, a white and very brittle mass of FeAs is obtained. The arsenide $FeAs_2$ occurs as the mineral löllingite in silver-white rhombic prisms. It is obtained artificially by heating finely powdered iron with the vapour of arsenic under pressure.[1] This artificial product, heated in a current of hydrogen, yields the arsenide FeAs as a silver-white, crystalline powder. The study of the freezing points of alloys of iron and arsenic indicates the existence of other arsenides, viz. :—Fe_3As_2, Fe_2As, and Fe_5As_4[2]. Mispickel or arsenical pyrites, FeAsS, crystallises in short rhombic prisms of a silver-white colour ; a portion of the iron is frequently replaced by cobalt, and this mineral serves as the chief source of arsenic compounds.

Ferric Arsenite.—The basic salt, $Fe_4O_5(OH)_5As=4Fe_2O_3$, $As_2O_3,5H_2O$, is a voluminous brown precipitate closely resembling ferric hydroxide in appearance. It is obtained by adding an aqueous solution of arsenious oxide, or an arsenite, to ferric acetate.

Ferric Arsenates.—The normal arsenate occurs as scorodite, $Fe(AsO_4),2H_2O$, in brown rhombic vitreous crystals. Basic arsenates are also found in the mineral kingdom ; amongst these we have iron-sinter or pharmacosiderite, $3FeAsO_4,Fe(OH)_3$, $6H_2O$, which occurs crystallised in the regular system in green or brownish-green adamantine crystals. The acid arsenate, $2Fe_2(HAsO_4)_3,9H_2O$, is a white precipitate obtained by adding hydrogen disodium arsenate to a solution of ferric chloride. It is easily soluble in hydrochloric acid, and separates on evaporation as a white powder.

Iron and Boron.

569 *Borides of Iron.*—The compound FeB is formed when the vapour of boron chloride is passed over iron at a dull red heat, or when soft iron is heated with boron in the electric furnace. It is thus obtained as an amorphous powder, or in yellowish-grey

[1] Hilpert and Dieckmann, *Ber.*, 1911, **44**, 2378.
[2] Friedrich, *Metallurgie*, 1907, **4**, 129.

crystals of specific gravity 7·15.[1] Other borides, viz., Fe_2B and FeB_2, have been prepared by heating reduced iron and boron in a porcelain tube in a current of hydrogen or in the electric furnace.[2] These borides of iron are oxidised by moist air, and are dissolved by hot concentrated acids.

Iron and Carbon.

570 *Iron Carbide*, Fe_3C, has already been described under steel (p. 1215).

Ferrous Carbonate, $FeCO_3$, occurs naturally as spathic iron ore, which, however, contains larger or smaller quantities of the carbonates of calcium, manganese, and magnesium. The mineral is obtained artificially in microscopic rhombohedra by precipitating a solution of green vitriol with sodium bicarbonate and heating the mixture for twelve to thirty-six hours at a temperature of 150° (Sénarmont). When a cold solution of pure ferrous sulphate is treated with sodium carbonate, a flocculent white precipitate is thrown down which rapidly becomes dirty green from absorption of oxygen and evolution of carbon dioxide, and is at last converted wholly into ferric hydroxide. If the precipitate is washed in total absence of air, it may be obtained pure and colourless, but usually it is a greyish powder, readily oxidised on exposure to air. If the moist precipitate is mixed with sugar it does not undergo such rapid change.

Ferrous bicarbonate exists in many mineral waters, and is formed in solution by the action of carbonic acid on ferrous carbonate. When such a solution is exposed to the air, carbon dioxide is evolved, and ferric hydroxide deposited. A quantitative study of the rate of oxidation of ferrous bicarbonate has shown that the reaction is of the first order.[3]

Ferric Carbonate is not known in the dry state, since the precipitate produced by the addition of a soluble carbonate to a ferric salt rapidly loses carbon dioxide.

Ferropentacarbonyl, $Fe(CO)_5$, was first obtained by Mond, Quincke, and Langer[4] by allowing iron prepared by the reduction of ferrous oxalate to stand in contact with carbonic

[1] Moissan, *Compt. rend.*, 1895, **120**, 173. Compare *Compt. rend.*, 1894, **119**, 1172.

[2] Jassonneix, *Compt. rend.*, 1907, **145**, 121. Compare Hoffmann, *Chem. Zeit.*, 1910, **34**, 1349.

[3] Just, *Ber.*, 1907, **40**, 3695.

[4] *Journ. Chem. Soc.*, 1891, **59**, 604, 1090.

oxide, and is evolved when the product is heated to 120°. Dewar and Jones[1] describe it as a viscous, pale yellow liquid, which forms a yellow crystalline solid at −20°, the latter becoming colourless at the temperature of liquid air. It has a specific gravity of 1·46, and boils at 102·5°. The vapour decomposes slowly below 180°, but rapidly deposits a mirror of metallic iron above that temperature. The vapour density at 129°, and the cryoscopic determination of the molecular weight in benzene solution, both agree with the molecular formula $Fe(CO)_5$.

Ferropentacarbonyl is decomposed by chlorine, with formation of ferrous and ferric chlorides and carbonic oxide, and by concentrated nitric and sulphuric acids, the latter yielding ferrous sulphate, hydrogen, and carbonic oxide:

$$Fe(CO)_5 + H_2SO_4 = FeSO_4 + 5CO + H_2.$$

It is very sensitive to the action of air and moisture, the liquid quickly depositing a reddish-brown precipitate on exposure to the atmosphere.

When ferropentacarbonyl, either alone or dissolved in dry ether or light petroleum, is exposed to sunlight at the ordinary temperature, it darkens, carbonic oxide being evolved and *diferro-nonacarbonyl*, $Fe_2(CO)_9$, formed:

$$2Fe(CO)_5 = Fe_2(CO)_9 + CO.$$

The reaction however, is reversible, and ferropentacarbonyl which has been exposed to light becomes colourless on standing in the dark. Rise of temperature favours the reverse reaction, and no decomposition takes place when ferropentacarbonyl is exposed to light at temperatures above 60°.

Diferrononacarbonyl crystallises in lustrous orange hexagonal plates which are quite stable in dry air, and have a specific gravity of 2·085 at 18°. It is practically insoluble in light petroleum and benzene, slightly soluble in alcohol and acetone, and more readily in pyridine. When heated it decomposes as follows:

$$Fe_2(CO)_9 = Fe(CO)_5 + Fe + 4CO.$$

Ferrotetracarbonyl, $Fe(CO)_4$.—When a solution of diferrononacarbonyl in ether or toluene is heated to 50°, it assumes an intensely green colour, and dark-green lustrous tablets with the

[1] *Proc. Roy. Soc.*, A., 1905, **76**, 558; 1907, **79**, 66.

empirical formula, $Fe(CO)_4$ are deposited. This substance is very stable at the ordinary temperature, but decomposes at 140–150° into iron and carbonic oxide. It dissolves in many organic solvents, forming dark-green solutions which very readily undergo oxidation. Attempts to determine the molecular weight in benzene solution showed that the substance must be a polymeride containing many $Fe(CO)_4$ groups, possibly $[Fe(CO)_4]_{20}$.

Iron and Cyanogen.

571 No simple cyanide of iron has yet been obtained, and probably these do not exist, owing to their great tendency to form complex cyanides. Several substances have been described as *ferrous cyanide*, $FeCy_2$, but have proved on investigation to be ferrocyanides of iron. Hydrocyanic acid gives no precipitate with solutions of ferrous salts, and on addition of ammonia a ferrous ammonium ferrocyanide, $(NH_4)_2Fe^{II}Fe^{II}Cy_6$, is formed which rapidly oxidises to the corresponding ferric salt, $NH_4Fe^{III}Fe^{II}Cy_6$.[1] *Ferric Cyanide*, $FeCy_3$, also appears to be incapable of existence. On addition of potassium cyanide to a solution of ferric salt, ferric hydroxide is precipitated, and hydrocyanic acid remains in solution.

572 Our knowledge of the complex compounds of iron and cyanogen commences with the discovery of Prussian blue in 1704 by a colourmaker named Diesbach. In 1752 Macquer observed that when this colour is boiled with caustic potash, oxide of iron remains, whilst a peculiar salt enters into solution which was named phlogisticated alkali, or yellow prussiate of potash. This body was shown to contain iron and prussic acid by Berthollet in 1787. Proust, in 1806, next found that iron remains in combination with prussic acid when the alkali in the yellow prussiate is replaced by other bases; and Ittner in 1809 considered that the compounds of ferric oxide and other bases with prussic acid are double salts. In opposition to this view, Porrett[2] described experiments from which he drew the conclusion that the so-called double prussiates containing iron are simple salts of a compound acid containing ferrous oxide and prussic acid. This he called *ferruretted chyazic acid*, a name based on the fact that it is a compound of carbon, hydrogen, and azote or nitrogen. Gay-Lussac's classical

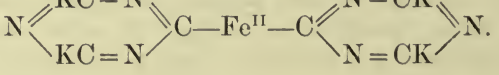
[1] Hofmann, *Annalen*, 1907, **352**, 54.

[2] *Phil. Trans.*, 1814, 527; *Ann. Phil.*, 1818, **12**, 214; 1819, **14**, 295.

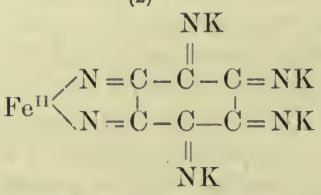
investigation of prussic acid followed immediately on Porrett's memoir. In this he proved that the acid is a hydrogen compound of the radical cyanogen. Berzelius then showed that all the salts of iron and prussic acid may be considered to be double cyanides, and that (according to our present nomenclature) the prussiate of potash is a cyanide of iron and potassium, $Fe(CN)_2,4KCN$. Three years later Gmelin,[1] by acting upon this salt with chlorine, obtained a new compound which, from its colour, was termed red prussiate of potash. This may be regarded as the ferric double salt, $Fe(CN)_3,3KCN$. Gmelin likewise proved that the potassium in the salt may be replaced by hydrogen, thus giving rise to ferricyanic acid. In the following year Gay-Lussac pointed out that the yellow prussiate may be supposed to contain a compound radical consisting of iron and cyanogen, to which he gave the name *cyanoferre*. Liebig extended this explanation to the other cyanogen compounds containing iron, and considered the above salts as compounds of two isomeric radicals FeC_6N_6, to which he gave the names of *ferrocyanogen* and *ferricyanogen*.

Many suggestions have been made as to the constitution of these two radicals. Graham [2] and Erlenmeyer [3] assumed these compounds to contain the radical of cyanuric acid, C_3N_3, on which supposition potassium ferrocyanide would have the constitutional formula (1), whilst Friedel [4] suggested the formula (2), and Browning [5] that given under (3):

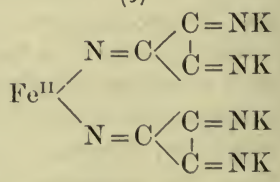
(1)



(2)



(3)



According to these various hypotheses, the ferrocyanides contain closed chains either of carbon atoms alone, or of carbon and nitrogen atoms. No evidence, however, has been obtained

[1] *Schweiggers' Journ.*, 1822, **34**, 325.
[2] *Elements of Chemistry*, 1850, i, 200. [3] *Lehrbuch Org. Chem.*, 1867, 148.
[4] *Compt. rend.*, 1887, **104**, 995. [5] *Journ. Chem. Soc.*, 1900, **77**, 1238.

in support of any of these views, and the general properties of the substances are quite distinct from those of the numerous compounds known to contain such closed chains. Moreover, one of the six cyanogen radicals can be replaced by numerous other radicals without any great alteration in general properties, which would not be the case if any of the above formulæ were correct. It is noteworthy that in the methyl ferrocyanides the methyl groups appear to be directly linked to nitrogen, and not to carbon.[1]

Analogous complex cyanides are formed by other metals of the eighth periodic group, and by metals occupying positions near them in the periodic table, such as chromium, *i.e.* by those metals which yield complex bases with ammonia, &c., and there is little doubt that these complex bases and the complex cyanides are compounds of the same order. The co-ordination theory of Werner (p. 36), which has thrown much light on the relations of the complex bases, is also of great value in making clear the similar relations of the ferrocyanides and analogous compounds.

According to this hypothesis, the iron atom occupies the centre of the system and is combined with the six cyanogen radicals which are "co-ordinated" with it. The complex radical thus formed is of an acid nature and is capable of combining with basic elements or groups which form cations in solution. Thus potassium ferrocyanide and ferricyanide are formulated as follows, the co-ordinated group being enclosed in square brackets: for the sake of shortness and simplicity the symbol Cy is used for the cyanogen radical CN:

Potassium Ferrocyanide	*Potassium Ferricyanide*
$K_4[Fe^{II}Cy_6]$.	$K_3[Fe^{III}Cy_6]$.

The ferrocyanogen radical is tetracidic, two of the cyanogen valencies being neutralised by the ferrous iron atom, whilst the ferricyanogen radical is triacidic, as the ferric iron atom neutralises the valency of three cyanogen groups.

One of the six cyanogen groups may be replaced in both ferro- and ferricyanides by a large number of other groups, including CO, NO, NO_2, NH_3, H_2O, SO_3, yielding substances which closely resemble the original salts in general properties. If the replacing group be a monovalent acid radical, such as NO_2, the valency of the group remains unchanged, whilst a divalent acid

[1] Hartley, *Journ. Chem. Soc.*, 1911, **99**, 1549.

radical increases the valency of the group by one unit, and a neutral substance reduces it by one unit. The nitroso-group and ammonia behave in this connection as neutral substances. Thus, sodium carbonylferrocyanide is $Na_3[Fe^{II}(CO)Cy_5]$; sodium nitrosoferricyanide (nitroprusside), $Na_2[Fe^{III}(NO)Cy_5]$; sodium sulphitoferrocyanide, $Na_5[Fe^{II}(SO_3)Cy_5]$; and sodium nitroferrocyanide, $Na_4[Fe^{II}(NO_2)Cy_5]$.

Ferrocyanogen Compounds.

573 Until recent years the ferrocyanides served as the point of departure for the preparation of almost all the other cyanogen compounds, and they are still manufactured on the large scale, although the cyanides specially required for the extraction of gold are at present largely obtained in other ways. Formerly, the only ferrocyanides obtained on the large scale were those of potassium and iron, but at present the sodium and calcium salts also are prepared in quantity.

The method formerly adopted for the manufacture of potassium ferrocyanide, and now obsolete, consisted in heating crude potashes in a cast iron pan, and adding from time to time a mixture of iron filings and nitrogenous organic matter (horns, feathers, dried blood, etc.). The fused mass was allowed to cool, and then lixiviated with warm water, ferrocyanide being obtained by the evaporation of this aqueous extract.[1]

Ferrocyanides are now obtained as by-products in the coal-gas manufacture and other industries in which coal is subjected to destructive distillation. The unpurified gas usually contains a small quantity of cyanogen compounds, chiefly if not entirely as hydrocyanic acid. When the gas is purified by means of ferric oxide (Vol. I., p. 871), this is partially absorbed, together with the sulphuretted hydrogen, and when the absorbing oxide is completely spent it is frequently found to contain sufficient Prussian blue to repay the cost of extraction.

A common method of obtaining the ferrocyanide from the spent oxide is to treat it with hot milk of lime, which converts the Prussian blue into calcium ferrocyanide; on addition of potassium or ammonium chloride to the filtered extract the sparingly soluble potassium calcium or ammonium calcium

[1] For full details of this and the modern methods of obtaining ferrocyanides, see the article on "Cyanides" in Thorpe's *Dictionary of Applied Chemistry*, vol. ii., 1912.

ferrocyanide, CaK_2FeCy_6 or $Ca(NH_4)_2FeCy_6$, separates out, and from this pure potassium or sodium ferrocyanide can readily be prepared.

In recent years the hydrocyanic acid has been extracted at a number of gas works by passing the gas, previous to the dry purification (Vol. I., p. 875), through a suitable apparatus in which it is brought into intimate contact with an alkaline liquid, to which an iron salt has been added. The latter is converted into ferrous sulphide by the action of the sulphuretted hydrogen in the crude gas, and this is acted on by the hydrocyanic acid in presence of alkali (*e.g.* potash) as follows:

$$FeS + 6HCy + 2K_2CO_3 = K_4FeCy_6 + H_2S + 2CO_2 + 2H_2O.$$

The potash may be replaced by sodium carbonate or lime, in which case sodium or calcium ferrocyanide is obtained.

If the gas is treated with a solution of ferrous sulphate previous to the removal of ammonia, the latter supplies the necessary alkali, and the hydrocyanic acid is absorbed and converted partly into ammonium ferrocyanide and partly into insoluble double ferrocyanides of ammonium and iron, the latter being almost the sole product when excess of ferrous sulphate is used. This is filtered and converted into soluble ferrocyanides by boiling with alkalis, the ammonia evolved being recovered as sulphate by absorption in sulphuric acid.

Ferrocyanides are now prepared also from thiocyanates, the latter being either made synthetically from carbon disulphide or recovered from crude coal-gas (Vol. I., p. 875). The thiocyanate is fused in pots and completely dried by passing through it a current of inert gas, and then heated with dry iron borings free from rust, air being excluded:

$$6NaCyS + 6Fe = 6NaCy + 6FeS.$$

The melt is then treated with water and boiled up with steam in a vat, when sodium ferrocyanide is formed together with sodium sulphide:[1]

$$6NaCy + FeS = Na_4FeCy_6 + Na_2S.$$

Hydrogen Ferrocyanide or *Ferrocyanic Acid*, $H_4Fe^{II}Cy_6$. This is best obtained when pure hydrochloric acid is added to an equal volume of a cold saturated solution of potassium ferrocyanide. The precipitate which forms is dried on a porous

[1] *J. Soc. Chem. Ind.*, 1895, **14**, 656.

plate in absence of air, then dissolved in alcohol, and precipitated by ether.[1] It is a white powder crystallising in small needles. Larger crystals may be obtained by pouring a layer of ether on to the alcoholic solution. Ferrocyanic acid is easily soluble in water and alcohol. It possesses a strongly acid taste and reaction, and liberates not only acetic, but even oxalic acid, from its salts. It oxidises quickly on exposure to air, especially when warmed, forming hydrocyanic acid and ferric ferrocyanide:

$$7H_4FeCy_6 + O_2 = 24HCy + Fe_7Cy_{18} + 2H_2O.$$

This reaction is employed in calico-printing, the cloth being printed with a mixture of tartaric acid and yellow prussiate, and then steamed.

When the solution of the acid is boiled, hydrocyanic acid is evolved and a white precipitate of ferrous hydrogen ferrocyanide remains behind:

$$2H_4[Fe^{II}Cy_6] = 6HCy + H_2Fe^{II}[Fe^{II}Cy_6].$$

When heated at 300° in absence of air it yields a pale yellow powder having the composition $FeCy_2$[2]; this is, however, not the simple cyanide, but more probably a ferrous ferrocyanide, $Fe^{II}_2(Fe^{II}Cy_6)$. Ferrocyanic acid also yields an *ethyl* derivative, $(C_2H_5)_4FeCy_6$, the molecular weight of which in aqueous solution is in accordance with the formula just given.[3] The acid forms crystalline compounds with ether, ethyl acetate, and other organic esters.[4]

Potassium Ferrocyanide or *Yellow Prussiate of Potash*, $K_4FeCy_6,3H_2O$.—The commercial manufacture of this salt has been described above. It is obtained also when a ferrous salt is added to potassium cyanide; a brown precipitate of uncertain composition is first formed, but quickly dissolves in excess of potassium cyanide yielding potassium ferrocyanide. The latter is formed also by the action of potassium cyanide solution on metallic iron in absence of air, slowly in the cold and quickly on heating:

$$6KCy + Fe + 2H_2O = K_4FeCy_6 + 2KOH + H_2.$$

Potassium ferrocyanide forms tetragonal pyramids, sp. gr. 1·83, in which the basal faces are usually dominant. They are of a

[1] Liebig, *Annalen*, 1853, **87**, 127.
[2] Browning, *Journ. Chem. Soc.*, 1900, **77**, 1234.
[3] Buchböck, *Zeit. physikal. Chem.*, 1897, **23**, 157.
[4] Browning, *loc. cit.*; Baeyer and Villiger, *Ber.*, 1901, **34**, 2679.

lemon-yellow colour and generally opaque. Small crystals, on the other hand, are amber-coloured and transparent. It has been maintained that this difference in colour has nothing to do with the size of the crystals, but is connected with the existence of two isomeric forms of the salt, which differ slightly also in density and solubility.[1] Potassium ferrocyanide does not undergo alteration in pure air at the ordinary temperature, but when heated to 60° it begins to lose its water of crystallisation, which is removed completely at 110°, the anhydrous salt remaining as a white powder. It has a sweetish, saline, and somewhat bitter taste, and is not poisonous, acting in large doses as an aperient. 100 parts of water dissolve about 38·5 parts of K_4FeCy_6 at 15°, and about 87 parts at 100°, but it is insoluble in alcohol even when the latter is considerably diluted with water. When its solution is exposed to light for some time Prussian blue separates out, and on long-continued boiling of the solution in the air ammonia is given off and the liquid becomes alkaline. The commercial salt frequently contains considerable quantities of potassium sulphate which can be removed by recrystallisation only with difficulty.

Potassium ferrocyanide, in addition to its use in the preparation of Prussian blue and other cyanogen compounds, is employed in calico-printing, and also for the case hardening of iron..

Sodium Ferrocyanide or *Yellow Prussiate of Soda*, Na_4FeCy_6, $10H_2O$, is manufactured in the manner already described, and may be obtained also by boiling Prussian blue with caustic soda or sodium carbonate. It crystallises readily in large monoclinic prisms, and effloresces slightly in the air; at 110° it loses the whole of the water, the residue being a white powder. 100 parts of water dissolve about 27 parts of $Na_4FeCy_6,10H_2O$ at 15°, and about 160 parts at 100°.

Ammonium Ferrocyanide, $(NH_4)_4FeCy_6,3H_2O$, is obtained by the action of ammonia on ferrocyanic acid or on Prussian blue, and crystallises in yellow prisms isomorphous with the potassium salt. Its solution decomposes readily on heating, with evolution of ammonium cyanide.

Calcium Ferrocyanide, $Ca_2FeCy_6,12H_2O$, is formed when Prussian blue is boiled with the requisite quantity of milk of lime, or by passing hydrogen cyanide into a mixture of slaked

[1] Briggs, *Journ. Chem. Soc.*, 1911, **99**, 1019.

lime and ferrous hydroxide suspended in water. It forms pale yellow, triclinic prisms; one part dissolves in 0·66 part of water at 90°, and it is even more soluble in cold water. The salt is very efflorescent and the analytical results for the water of crystallisation are always somewhat lower than are required for $12H_2O$.[1] Measurements of the osmotic pressure and electrical conductivity of aqueous solutions of calcium and strontium ferrocyanides have indicated that these salts are associated in solution.[2]

Potassium Calcium Ferrocyanide, $K_2CaFeCy_6,3H_2O$, and *Ammonium Calcium Ferrocyanide*, $(NH_4)_2CaFeCy_6,3H_2O$, are obtained as white crystalline precipitates, very sparingly soluble in water, when calcium chloride is added to a moderately concentrated solution of potassium or ammonium ferrocyanide, or by the addition of potassium or ammonium chloride to a solution of calcium ferrocyanide.

Strontium Ferrocyanide, $Sr_2FeCy_6,14H_2O$, is most readily obtained by neutralising ferrocyanic acid with strontium hydroxide or carbonate. It is very soluble in water, and crystallises from concentrated solution in monoclinic prisms, which lose $7H_2O$ on standing in the air, and a further $6H_2O$ over sulphuric acid.

Barium Ferrocyanide, $Ba_2FeCy_6,6H_2O$, is obtained by boiling Prussian blue with baryta water, or by the action of ferrous sulphate on barium cyanide. It forms flat monoclinic prisms which dissolve in 580 parts of cold, and 116 parts of boiling water.

Barium Potassium Ferrocyanide, $K_2BaFeCy_6,3H_2O$.—This salt is deposited in small yellow rhombohedra when boiling saturated solutions of 2 parts of potassium ferrocyanide and 1 part of barium chloride are mixed, and the mixture allowed to cool. It dissolves in 38 parts of cold, and 9·5 parts of boiling water.

Magnesium Ferrocyanide, $Mg_2FeCy_6,12H_2O$, is prepared in a similar manner to the calcium salt, and crystallises in pale yellow needles which are exceedingly soluble in water. The crystals lose $5H_2O$ on standing in the air.

Zinc Ferrocyanide, Zn_2FeCy_6, is a white precipitate used in medicine.

[1] Colman, *Analyst*, 1910, **35**, 299. Compare Berkeley, Hartley, and Burton, *Phil. Trans.*, 1909, **209**, 180.

[2] Berkeley, Hartley, and Stephenson, *Phil. Trans.*, 1909, **209**, 319.

Copper Ferrocyanide, Cu_2FeCy_6+aq, is a fine brown precipitate known as Hatchett's brown. If solutions of $CuSO_4$ and K_4FeCy_6 are allowed to come into contact without mixing, copper ferrocyanide is formed as a thin membrane at the common surface. This membrane is permeable to water, but impermeable to various dissolved substances, and on this ground has been extensively employed in the investigation of osmotic pressure.[1]

A large number of other ferrocyanides and double ferrocyanides have been prepared, many of which crystallise well.[2] Those of the heavy metals are mostly sparingly soluble or insoluble precipitates, some of which possess characteristic colours, as in the case of copper and uranium, and potassium ferrocyanide is therefore used as a reagent for these metals. The ferrocyanides of iron are described below.

Ferricyanogen Compounds.

574 *Ferricyanic Acid*, H_3FeCy_6.—This is obtained by decomposing the lead salt with dilute sulphuric acid, and evaporating the solution at a moderate temperature. The acid crystallises in brown needles and has an astringent acid taste.

Potassium Ferricyanide, K_3FeCy_6, is frequently termed *red prussiate of potash*, and is formed when potassium ferrocyanide is treated with oxidising agents. It is obtained on the large scale by passing chlorine into a solution of the yellow prussiate:

$$2K_4FeCy_6+Cl_2=2K_3FeCy_6+2KCl.$$

By repeated crystallisation it may be readily separated from the potassium chloride formed at the same time, and is obtained as large dark-red anhydrous monoclinic prisms, sp. gr. 1·8, which occur frequently in twin forms. Potassium ferricyanide possesses a faintly astringent and saline taste, and dissolves in water giving a yellowish-brown solution, which on dilution assumes a lemon-yellow colour. One hundred parts of water dissolve:[3]

At	4·4°	10°	15·6°	37·8°	100°
K_3FeCy_6	33·0	36·6	39·7	58·8	77·6,

[1] Traube, *Archiv für Anatomie und Physiologie*, 1867, 124; Pfeffer, *Osmotische Untersuchungen* (Leipzig, 1877); Morse, *Amer. Chem. J.*, 1911, **45**, 558.

[2] Wyrouboff, *Ann. Chim. Phys.*, 1869, [4], **16**, 280; 1870, [4], **21**, 271; 1876, [5], **8**, 444; Messner, *Zeit. anorg. Chem.*, 1895, **8**, 368.

[3] Wallace, *Journ. Chem. Soc.*, 1855, **7**, 80.

and 82 parts at 104°, the boiling point of the saturated solution. It is only slightly soluble in alcohol. When exposed to light the solution becomes darker, and a blue precipitate is formed, potassium ferrocyanide remaining in solution. When the salt is heated in a flame it burns, and when mixed with ammonium nitrate and heated, the mixture detonates. It is a powerful oxidising agent, especially in alkaline solution, converting the monoxides of lead and manganese into dioxides, and forming potassium chromate and potasssium ferrocyanide when boiled with a solution of chromium sesquioxide in potash :

$$6K_3FeCy_6 + Cr_2O_3 + 10KOH = 6K_4FeCy_6 + 2K_2CrO_4 + 5H_2O.$$

In solution it is reduced to ferrocyanide by sodium amalgam, and by hydrogen dioxide, oxygen being evolved in the latter case :

$$4K_3FeCy_6 + 2H_2O_2 = 3K_4FeCy_6 + H_4FeCy_6 + 2O_2.$$

According to Locke and Edwards[1] an isomeric form of potassium ferricyanide exists, which forms olive-coloured crystals having the composition K_3FeCy_6,H_2O. The solution of this salt yields precipitates with salts of the heavy metals which are not identical with those obtained in the same way from ordinary ferricyanide. On reduction with sodium amalgam, however, it yields, like the ordinary salt, potassium ferrocyanide.

Sodium Ferricyanide, $2Na_3FeCy_6,H_2O$, is obtained by the action of chlorine upon sodium ferrocyanide. It dissolves in 1·25 parts of boiling, and 5·3 parts of cold water, and crystallises in ruby-red four-sided prisms which deliquesce on exposure to air.

Ammonium Ferricyanide, $2(NH_4)_3FeCy_6,H_2O$, is obtained in a similar way to the other ferricyanides. It forms fine red monoclinic prisms, easily soluble in water and permanent in the air.

Lead Ferricyanide, $Pb_3(FeCy_6)_2,16H_2O$, is formed by mixing hot solutions of the potassium salt and lead nitrate. It forms dark reddish-brown crystals slightly soluble in cold, and rather more soluble in hot water.

The ferricyanides of most of the other heavy metals are precipitates, generally possessing a yellow, greenish-brown, or red-

[1] *Amer. Chem. J.*, 1899, **21**, 193.

dish-brown colour, whilst some of them, like that of tin, are colourless.

Ferro- and Ferri-cyanides of Iron.

575 As already mentioned (p. 1249) the double cyanides of iron were the earliest known cyanogen compounds, having been first obtained in 1704. In spite, however, of much experimental work by Berzelius, Liebig, Williamson, and others, the exact composition and constitution of the various compounds formed by the interaction of ferro- and ferri-cyanides with ferrous and ferric salts is still in many respects doubtful. This is largely owing to the fact that the preparation of these compounds in a state of purity is very difficult, and, moreover, slight alterations in the conditions under which the interaction of iron salts and the ferrocyanides takes place have frequently a very great influence on the nature of the product.

576 *Ferrous Ferrocyanides.*—When ferrous sulphate is added to potassium ferrocyanide in cold neutral solution in absence of oxygen, a white precipitate is obtained having the composition $Fe^{II}K_2[Fe^{II}Cy_6]$. This oxidises with great rapidity in the air, yielding the β-soluble blue described below. In acid solution a precipitate of similar composition is formed,[1] which, however, differs from the foregoing in being less readily oxidised, and yielding γ-soluble blue (p. 1262).

A third substance of the same composition is obtained as an insoluble compound in the preparation of hydrocyanic acid by the action of sulphuric acid on potassium ferrocyanide (Vol. I., p. 840):

$$2K_4FeCy_6 + 3H_2SO_4 = 3K_2SO_4 + K_2Fe^{II}[Fe^{II}Cy_6] + 6HCy.$$

It forms a pale-yellow powder which is seen under the microscope to consist of doubly refractive crystals of a pale-greenish colour. It is much less readily oxidised than either of the other compounds already described, but when treated with nitric acid or hydrogen dioxide is converted into Williamson's violet (p. 1263).

Ferrous Hydrogen Ferrocyanide, $H_2Fe^{II}[Fe^{II}Cy_6]$, corresponding to the last named salt, is obtained by heating ferrocyanic acid solution at 110–120°, and on oxidation yields a

[1] Compare Müller and Treadwell, *J. pr. Chem.*, 1909, [ii], **80**, 170.

violet substance, $Fe^{III}H[Fe^{II}Cy_6]$, closely resembling Williamson's violet in appearance, but containing no alkali.

577 *Ferric Ferrocyanides.*— These substances are the most important of the iron-cyanogen derivatives, the various substances comprised under the general name of Prussian blue belonging to this class. They are obtained (1) by the interaction of ferric salts and ferrocyanides; (2) by the interaction of ferrous salts and ferricyanides; (3) by the oxidation of ferrous ferrocyanides; and (4) by the reduction of ferric ferricyanides. The compounds formed in the different ways, although they may have the same empirical composition, frequently differ in both physical and chemical properties.

The researches of Hofmann[1] have shown that all these compounds consist of ferrocyanic acid, in which the hydrogen is either wholly or partially replaced by ferric iron, or partly by ferric iron and partly by another metal, and all of them may be represented by one of the two simple formulæ: (1) $Fe_4^{III}[Fe^{II}Cy_6]_3$, and (2) $Fe^{III}X[Fe^{II}Cy_6]$, where X is either hydrogen or a monovalent metal. The molecular weight is, however, undoubtedly much higher than that shown by the simple formulæ just given, and the products having the same empirical composition but different chemical and physical properties are, in all probability, polymeric modifications of the molecule represented by the simple formula.

With the single exception of one of the ferric ammonium ferrocyanides none of these compounds has been obtained anhydrous or in the crystalline form. The remainder are all colloidal substances, which still retain water when dried for months over phosphorus pentoxide, and this water cannot be removed by heat without simultaneous decomposition of the compound. On account of their colloidal nature, it is extremely difficult to prepare them in a state of purity, as like other similar substances they obstinately retain salts, and on this account very varying formulæ have been attributed to them in the past by various workers.

All the ferric ferrocyanides possess an intensely blue or violet colour, and form valuable dyes, differing in this respect from all the other ferrocyanides, for although most of the latter are coloured, none of them can be described as colouring matters. Hofmann and Resenscheck[2] suggest that the cause of the

[1] *Annalen*, 1904, **337**, 1; 1905, **340**, 267; 1905, **342**, 364; 1907, **352**, 54; *J. pr. Chem.*, 1909, [ii], **80**, 150. [2] *Annalen*, 1905, **342**, 364.

intense colour is the presence in the same molecule of ferrous and ferric iron atoms, and point out that similar intense colour is present in many other compounds containing the same element in different states of oxidation, as in sulphur sesquioxide, red lead, and the tungsten bronzes. It has also been supposed that the presence of chemically combined water was essential to the production of the colour, but the preparation of an anhydrous ferric ammonium ferrocyanide by Hofmann and Arnoldi [1] disproves this suggestion, as that substance is still intensely coloured.

α-Soluble Prussian Blue or *α-Ferric Potassium Ferrocyanide*, $4Fe^{III}K[Fe^{II}Cy_6],7H_2O$, is obtained by precipitating a solution of potassium ferrocyanide with slightly less than one equivalent of a ferric salt; the precipitate is washed by decantation with potassium chloride solution, and then with 70 per cent. alcohol, and dried over phosphorus pentoxide. It forms a voluminous mass, having a beautiful bronze reflex, and yields a deep-blue powder. It dissolves in pure water forming a deep-blue solution, and like other colloids is precipitated by the addition of salts. It also dissolves readily in oxalic acid and is quickly converted into ferrocyanide and ferric hydroxide by dilute ammonia. The water in the dried substance cannot be driven off without decomposition taking place, and is therefore probably "constitutional" water. Hofmann states that it is in all probability a basic ferric salt of the simplest formula $(HO)_2Fe^{III}[Fe^{II}Cy_6]KH_2$, two molecules of which have lost one molecule H_2O, forming the anhydro-salt:

$$KH_2[Fe^{II}Cy_6]Fe^{III}(OH).O.(HO)Fe^{III}[Fe^{II}Cy_6]KH_2.$$

When treated with dilute acid it loses potassium, yielding the corresponding *α-ferric hydrogen ferrocyanide*, $Fe^{III}H[Fe^{II}Cy_6]$ + aq., which closely resembles the ferric potassium salt, but is insoluble in water.

When a solution of potassium ferricyanide is precipitated with slightly less than one equivalent of ferrous salt a soluble Prussian blue is produced, which its mode of formation would indicate to be a ferrous potassium ferricyanide, $Fe^{II}K[Fe^{III}Cy_6]$. It has, however, been shown by Skraup,[2] and by Hofmann, Heine, and Höchtlen,[3] that this substance is identical with that obtained in the manner already described from potassium

[1] *Ber.*, 1906, **39**, 2204.
[2] *Annalen*, 1877, **186**, 371.
[3] *Annalen*, 1904, **337**, 1.

ferrocyanide and a ferric salt. Evidence other than that of the method of formation is therefore necessary to decide whether the substance possesses the constitution (1) or (2).

(1)	(2)
Ferric Potassium Ferrocyanide.	*Ferrous Potassium Ferricyanide.*
$Fe^{III}K[Fe^{II}Cy_6]$.	$Fe^{II}K[Fe^{III}Cy_6]$.

Alkalis decompose it into potassium ferrocyanide and ferric hydroxide, which is in favour of the first formula, but this is not conclusive, inasmuch as potassium ferricyanide and ferrous hydroxide, which would be the products formed from a substance of the second formula, immediately interact, yielding ferrocyanide and ferric hydroxide. Hofmann has, however, shown that dilute hydrogen dioxide containing acid, which readily reduces the ferricyanogen group to ferrocyanogen, but has no effect on ferric salts, quickly reduces a ferric ferricyanide solution to Prussian blue, and also oxidises the ferrous ferrocyanides to Prussian blue. This must therefore contain the ferric iron as the basic constituent, and ferrous iron in the acidic radical, as given in formula (1). In fact all the blue iron cyanogen compounds are ferr*ic* ferrocyanides, the ferr*ous* ferricyanides apparently not being capable of permanent existence, intramolecular change taking place where their formation would be expected.

β-Soluble Prussian Blue, $Fe^{III}K[Fe^{II}Cy_6],H_2O$, is obtained by the oxidation of the ferrous potassium ferrocyanide obtained in neutral solution (p. 1259). It is soluble in water, and differs from the previous compound chiefly by its insolubility in oxalic acid.

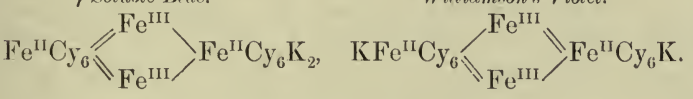
γ-Soluble Prussian Blue is prepared in a similar manner by oxidising the ferrous potassium ferrocyanide obtained in cold acid solution. It is soluble in water, but is much more stable towards alkalis than the two previous compounds, and only loses the potassium with difficulty by the action of dilute acids or of ferric chloride.

Williamson's Violet, $Fe^{III}K[Fe^{II}Cy_6],H_2O$.—This substance was first obtained by A. W. Williamson by the action of nitric acid or some other oxidising agent on the residue left in the preparation of hydrocyanic acid from potassium ferrocyanide (p. 1259). It forms a deep violet-blue powder, which is transparent in thin layers, allowing green light to pass through. It is much more stable than any of the three compounds already

described of the same empirical composition, being quite insoluble in mineral acids, which do not remove the potassium, and also in oxalic acid, and being only very slowly decomposed by dilute alkalis.

Hofmann regards γ-soluble blue and Williamson's Violet as formed by the union of two molecules of the simple substance $Fe^{III}K[Fe^{II}Cy_6]$, the former having an unsymmetrical and the latter a symmetrical constitution, as shown by the formulæ:

γ-Soluble Blue. *Williamson's Violet.*



In addition to the ferric potassium compounds, several ferric ammonium compounds have been prepared.

Monthiers' Blue, $Fe^{III}NH_4[Fe^{II}Cy_6],H_2O$, was first obtained by Monthiers[1] by the oxidation of the white precipitate formed by the action of ammoniacal ferrous chloride on potassium ferrocyanide, and given by him the formula $(Fe_2)_2(FeCy_6)_3,6NH_3,9H_2O$, but it has been shown by Hofmann, Arnoldi, and Hiendlmaier[2] to have the formula given above. It is also formed if any of the soluble Prussian blues be exposed to sunlight with ammonium oxalate solution, and the resulting white compound oxidised by hydrogen dioxide, but is most readily obtained by acting on a solution containing potassium ferrocyanide, ammonium chloride, and ammonia with iron wire, and oxidising the green precipitate with hydrogen dioxide. It is a deep-blue powder having an enamel-blue reflex, is soluble in water and oxalic acid, and is decomposed somewhat slowly by dilute alkalis.

A crystalline anhydrous *ferric ammonium ferrocyanide*, $Fe^{III}NH_4[Fe^{II}Cy_6]$, is obtained together with nitroprusside by heating a solution of hydroxylamine hydrochloride with one of potassium ferrocyanide, and forms a deep-blue insoluble powder, which is seen under the microscope to consist of opaque violet-red lustrous cubes. In its properties it very closely resembles Williamson's violet.[3]

Insoluble Prussian Blue, or *Ferric Ferrocyanide*, $Fe^{III}_4[Fe^{II}Cy_6]_3$ or Fe_7Cy_{18}, is prepared by precipitating a soluble ferrocyanide with an excess of ferric salt, or by the action of

[1] *J. Pharm.*, 1846, [3], **9**, 262. [2] *Annalen*, 1907, **352**, 54.
[3] Hofmann and Arnoldi, *Ber.*, 1906, **39**, 2204.

the latter on soluble Prussian blue. The exact composition of the precipitate depends on the proportions of ferric salt and ferrocyanide taken,[1] and it is exceedingly difficult to free it from the last traces of alkali. The precipitate is insoluble in water and dilute mineral acids, but dissolves in ammonium tartrate solution, forming a violet liquid, and in oxalic acid forming a blue solution. The latter was formerly largely used as a blue ink, but has now been replaced by the blue aniline colours.

The dried substance contains water which cannot be driven off without decomposition, the amount corresponding approximately to the formula, $Fe_7Cy_{18},9H_2O$, or $Fe_7Cy_{18},10H_2O$. When strongly heated in the air it burns like tinder forming ferric oxide, and it is decomposed by alkalis into ferric hydroxide and the ferrocyanide of the alkali employed. Concentrated sulphuric acid converts it into a white mass, neither iron nor hydrocyanic acid being removed, and when this is dried on a porous plate, an amorphous powder remains which is decomposed by water into Prussian blue and sulphuric acid (Berzelius). Prussian blue also dissolves in hot concentrated hydrochloric acid, forming a yellow solution from which ferrocyanic acid separates on standing. It dissolves more readily in a mixture of hydrochloric acid with ethyl alcohol or higher alcohols, or with amyl acetate, small quantities of water causing a blue precipitate in the solutions.[2]

Turnbull's Blue.—Gmelin obtained a blue compound by the precipitation of potassium ferricyanide with excess of ferrous salt, which was afterwards manufactured in England under the name of Turnbull's blue. From its mode of preparation it was supposed to be ferrous ferricyanide, $Fe_3^{II}[Fe^{III}Cy_6]_2$ or Fe_5Cy_{12}, but it has been found[3] that the compound thus formed, after it has been washed in presence of air, during which oxidation probably takes place, is identical with the insoluble Prussian blue obtained from ferric salts and ferrocyanides (see also p. 1260).

Another ferric ferrocyanide differing from that above described, has been obtained by Hofmann and Resenscheck by the action of hydrogen dioxide on a solution of ferric ferricyanide in presence of an excess of strong hydrochloric acid. It has the

[1] Volschin, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 480; Müller and Stanisch, *J. pr. Chem.*, 1909, [ii], **79**, 81; **80**, 153.

[2] Coffignier, *Bull. Soc. chim.*, 1902, [3], **27**, 696; Watson Smith, *J. Soc. Chem. Ind.*, 1903, **22**, 472.

[3] Hofmann, Heine, and Höchtlen, *Annalen*, 1904, **337**, 1. Compare, however, Müller and Stanisch, *J. pr. Chem.*, 1909, [ii], **79**, 81; **80**, 153.

composition $Fe_7Cy_{18}.10H_2O$, but in colour resembles Williamson's violet, and is insoluble in oxalic acid.

Commercial Prussian Blue is a mixture of a number of the ferric ferrocyanides above described, and consequently varies considerably in its colour and appearance. It is sold in the form of lumps, powder, and paste. All these have a deep blue colour and show a bronze reflex in varying degree. The finest variety, known as Paris blue, is obtained by the precipitation of potassium ferrocyanide by a ferric salt, and the lumps of this product, especially when wet, have a splendid bronze lustre. As ferric salts are dear, the blue is usually made by precipitating a ferrocyanide with ferrous salt, and oxidising the product by an oxidising agent such as bleaching powder. The exact conditions under which the preparation is carried out are, however, mostly kept secret by the makers.

Prussian blue is still employed as a dye, although to a less extent than formerly, having been to a considerable degree replaced by the coal-tar colours.

578 *Ferric Ferricyanides.*—When a ferric salt is added to a solution of a ferricyanide no precipitate is obtained, but the solution assumes a dark-brown colour, and probably contains ferric ferricyanide, although no solid compound of that composition has been isolated from it.

Prussian Green.—When an excess of chlorine is allowed to act on a solution of a ferro- or ferri-cyanide, or on Williamson's violet, a green hydrated compound is precipitated, to which the name Prussian green has been given. The composition of this substance is variable, and numerous formulæ have been proposed for it, such as Fe_3Cy_8, Fe_5Cy_{14}, Fe_9Cy_{24}. It has, however, been shown by Messner[1] that when chlorine is passed through a boiling solution in the dark, until no further action takes place, and the precipitate is washed with water in the dark, the green product has the empirical formula $FeCy_3$, and is probably a polymeric ferric ferricyanide, $[Fe^{III}(Fe^{III}Cy_6)]_x$. It readily loses cyanogen, forming Prussian blue, this being the cause of the varying composition found by the former investigators. It is doubtful whether the compound when pure has a green colour, this being probably due to the presence of traces of Prussian blue.

[1] *Zeit. anorg. Chem.*, 1895, **9**, 136.

Iron Pentacyano-Derivatives.

579 It has already been stated that one of the cyanogen groups in ferro- and ferri-cyanides can be replaced by other groups, forming stable salts, which in general properties are closely allied to these substances.

Carbonylferrocyanic Acid, $H_3[Fe^{II}(CO)Cy_5]$.—The *potassium* salt of this acid is slowly formed by the action of carbonic oxide on boiling potassium ferrocyanide solution, the group CO replacing 1 molecule of potassium cyanide, which undergoes conversion into potassium formate and ammonia:[1]

$$K_4FeCy_6 + CO + 2H_2O = K_3Fe(CO)Cy_5 + NH_3 + H.CO.OK.$$

It forms pale-yellow crystals containing $4H_2O$. The free acid forms colourless crystalline plates.

The salts of this acid are almost invariably present in the crude ferrocyanides obtained from coal-gas, their formation being due to the carbonic oxide always present in the gas. They are readily separated by treatment with dilute alcohol, in which the carbonylferrocyanides are soluble, and the ferrocyanides insoluble.[2]

With ferric chloride the carbonylferrocyanides give a precipitate of *ferric carbonylferrocyanide*, $Fe^{III}[Fe^{II}(CO)Cy_5]+aq.$, which differs from Prussian blue in possessing an intense purple colour. The *copper* salt is a pale apple-green precipitate.

Nitroprussic acid or *Nitrosoferricyanic Acid*, $H_2[Fe^{III}(NO)Cy_5]$. —Gmelin and other chemists observed that the coffee-brown solution obtained by the action of nitric acid on potassium ferrocyanide yields a splendid purple-red colour when treated with the sulphides of the alkalis. Playfair,[3] in 1849, showed that this reaction is produced by the presence of a peculiar compound which is formed by the action of nitric acid on ferro- or ferri-cyanides, which he termed nitroprussic acid, and which may be regarded as ferricyanic acid in which one of the Cy groups has been replaced by the nitroso-group NO.

[1] Muller, *Ann. Chim. Phys*, 1889, [6], **17**, 93; *Compt. rend.*, 1898, **126**, 1421.

[2] Compare Lecocq, *Bull. Soc. chim. Belg.*, 1911, **25**, 72.

[3] *Phil. Trans.*, 1849, **139**, 477.

The acid is formed when nitric oxide is passed into an acid solution of potassium ferrocyanide, the ferrocyanic acid being first oxidised to ferricyanic acid, upon which nitric oxide then acts as follows:

$$H_3FeCy_6 + NO = H_2[Fe(NO)Cy_5] + HCy.$$

The potassium salt is formed also by the action of potassium nitrite on a mixture of potassium cyanide and a ferrous salt:

$$5KCy + 2FeSO_4 + KNO_2 + H_2O = K_2[Fe(NO)Cy_5] + Fe(OH)_2 + 2K_2SO_4,$$

the ferrous hydroxide being further converted into ferric hydroxide,[1] with liberation of ammonia, by the action of the nitroprusside or the nitrite.

Nitroprussides may be prepared from either ferrocyanides or cyanides. In the former case powdered potassium ferrocyanide is treated with double its weight of strong nitric acid previously mixed with an equal volume of water. The coffee-coloured solution evolves carbon dioxide, nitrogen, cyanogen, and hydrocyanic acid, and as soon as solution is complete it is warmed on the water-bath till a portion of the liquid gives a slate-coloured precipitate with ferrous sulphate. On cooling, the liquor is poured off from the separated potassium nitrate, and neutralised with sodium carbonate. The solution is then concentrated, filtered, and the nitrates separated by fractional crystallisation, or the copper salt may be precipitated and decomposed, after washing, with soluble bases.

To obtain them from cyanides, a concentrated aqueous solution of ferrous sulphate is mixed with a solution of equal parts of potassium cyanide and sodium nitrite, and allowed to remain for five hours at the ordinary temperature. Ferric hydroxide separates, and nitrogen and nitric oxide are evolved. The solution is then heated to 25° for a short time, made slightly alkaline with caustic soda, filtered, and the salt obtained by crystallisation.

Nitroprussic acid is formed by decomposing the silver salt with hydrochloric acid, or the barium salt with dilute sulphuric acid. The red, strongly acid solution leaves on evaporation in a vacuum dark-red deliquescent prismatic needles. This com-

[1] Städeler, *Annalen*, 1869, **151**, 1.

pound is very unstable and partially decomposes during the concentration of the liquid with formation of ferric hydroxide, hydrocyanic acid, &c.

Potassium Nitroprusside, $K_2[Fe(NO)Cy_5]$, forms dark-red monoclinic prisms which deliquesce in the air and are readily soluble in water.

Sodium Nitroprusside, $Na_2[Fe(NO)Cy_5],2H_2O$, crystallises most readily of all the nitroprussides, and is usually prepared by concentrating the solution prepared as above described until a sufficient quantity of nitroprusside has crystallised out. This is then removed from the warm solution in order to avoid any admixture of nitrates. It is purified by crystallisation and forms large ruby-red rhombic prisms. It dissolves in 2·5 parts of water at 15°, and is more soluble in hot water. When exposed to light, the solution decomposes with separation of Prussian blue and nitric oxide. Boiled with caustic soda ferrous hydroxide is separated, sodium ferrocyanide and sodium nitrite being formed.

The nitroprussides of ammonium and of the alkaline earth metals also form red, easily soluble salts, their solutions decomposing on standing or on boiling, with separation of Prussian blue and ferric oxide. The silver salt and the ferrous salt are flesh-coloured precipitates.

The splendid purple colour which the nitroprussides impart to a solution of an alkaline sulphide is very characteristic, and this reaction is employed both for the detection of alkali sulphides and of small quantities of alkalis and alkaline earths in solution, by passing a little sulphuretted hydrogen through the liquid in the latter case and then adding a few drops of nitroprusside solution.

The purple compound thus produced is very unstable; its constitution is uncertain, but is very probably represented by the formula $Na_3[Fe^{II}(O{:}N.SNa)Cy_5]$, as Hofmann,[1] by the action of thiourea, $CS(NH_2)_2$, on sodium nitroprusside, has obtained the compound $Na_3[Fe^{II}(O{:}N.SCNH.NH_2)Cy_5]$, which forms a beautiful carmine-red powder, closely resembling in its properties the substance formed from nitroprussides and sulphides.

Starting from sodium nitroprusside, Hofmann has obtained the following substituted ferro- and ferri-cyanides:

[1] *Annalen*, 1900, **312**, 1; compare Virgili, *Zeit. anal. Chem.*, 1906, **45**, 409.

Sodium nitroferrocyanide,	$Na_4[Fe^{II}(NO_2)Cy_5],10H_2O$,
Potassium nitroferricyanide,	$K_3[Fe^{III}(NO_2)Cy_5]$,
Sodium aquoferrocyanide,	$Na_3[Fe^{II}(H_2O)Cy_5],7H_2O$,
Sodium aquoferricyanide,	$Na_2[Fe^{III}(H_2O)Cy_5]$,
Sodium ammonioferrocyanide,	$Na_3[Fe^{II}(NH_3)Cy_5],6H_2O$,
Sodium ammonioferricyanide,	$Na_2[Fe^{III}(NH_3)Cy_5],H_2O$,
Sodium sulphitoferrocyanide,	$Na_5[Fe^{II}(SO_3)Cy_5],9H_2O$,
Sodium arsenitoferrocyanide,	$Na_4[Fe^{II}(AsO_2)Cy_5],10H_2O$.

The substituted ferrocyanides are yellow or reddish-yellow crystalline salts, which give blue precipitates with ferric salts, and brownish-red precipitates with copper salts. The substituted ferricyanides have a deep carmine-red or purple colour, and give no precipitate with ferric salts, and pale-green precipitates with copper salts. All these compounds are converted into sodium ferrocyanide by boiling with sodium cyanide solution.

Iron Thiocyanates.

580 *Ferrous Thiocyanate*, $Fe(SCN)_2,3H_2O$, is obtained in large pale-green monoclinic crystals by dissolving iron wire in concentrated thiocyanic acid and evaporating the liquid in absence of air. The salt dissolves readily in water, alcohol, and ether, and becomes red-coloured on exposure to the air.

Ferric Thiocyanate, $Fe(SCN)_3,3H_2O$. — This compound is obtained in the pure state when a mixture of anhydrous ferric sulphate and potassium thiocyanate in equivalent proportions is treated with alcohol and the solution evaporated over sulphuric acid in a vacuum. Dark-red or almost black cubical crystals are deposited, and these dissolve readily in water, alcohol, and ether. If a concentrated aqueous solution is shaken with ether it becomes colourless and the ether attains a purple-red colour. The aqueous solution is also decolorised in presence of reducing agents as well as on treatment with mercuric chloride or gold chloride.

A solution of ferric thiocyanate is not permanent, and the colour gradually fades when the solution is allowed to stand at the ordinary temperature.[1] This bleaching is due to the progressive reduction of the iron to the ferrous condition, and it has been shown that in the corresponding oxidation of thio-

[1] See, for example, Oerum, *Zeit. anal. Chem.*, 1904, **43**, 152; Stokes and Cain, *J. Amer. Chem. Soc.*, 1907, **29**, 412, 445.

cyanate which occurs, carbon dioxide, sulphuric acid, and ammonia are formed.[1]

The reaction between a ferric salt and potassium thiocyanate in aqueous solution is not complete when equivalent quantities are employed, and the state of equilibrium which is produced in any mixture of the two depends on the degree of dilution, the temperature, and the relative proportion of the two salts present.[2] When the deep red solution is diluted so as to be almost colourless and potassium thiocyanate then added the deep-red colour is again produced.

The iron thiocyanates form double salts with other thiocyanates, which are analogous to the ferro- and ferri-cyanides, and have the general formulæ $M^{I}_{4}Fe(CNS)_{6}$ and $M^{I}_{3}Fe(CNS)_{6}$. Unlike these, however, they are very unstable substances and are completely dissociated by water into the constituent salts.[3]

Iron and Silicon.

581 *Silicides of Iron.*—Iron can readily be alloyed with silicon, and since silica and silicates are reduced by carbon in the presence of iron, all cast iron contains silicon, probably in the form of a silicide (p. 1187).

The compound Fe_2Si is obtained by heating iron with silicon in the electric furnace, and forms magnetic prisms of specific gravity 7. It is readily attacked by hydrofluoric acid,[4] and by sulphur chloride.[5]

Compounds of the formulæ FeSi, $FeSi_2$, and Fe_3Si_2 have also been described.[6]

Mixtures of iron and silicon, known as "ferro-silicon" and containing up to 90 per cent. silicon, are prepared in the electric furnace on a large scale. Under certain conditions ferro-silicon is liable to decompose, giving off poisonous gases.[7]

[1] Philip and Bramley, *Journ. Chem. Soc.*, 1913, **103**, 795.

[2] Krüss and Moraht, *Ber.*, 1889, **22**, 2061; *Zeit. anorg. Chem.*, 1892, **1**, 399; Magnanini, *Zeit. physikal. Chem.*, 1891, **8**, 1; Vernon, *Chem. News*, 1892, **66**, 177 *et seq.*; 1893, **67**, 66; Gladstone, *ibid.*, 1893, **67**, 1.

[3] Rosenheim and Cohn, *Zeit. anorg. Chem.*, 1901, **27**, 280.

[4] Moissan, *Compt. rend.*, 1895, **121**, 621.

[5] Nicolardot, *Compt. rend.*, 1908, **147**, 676.

[6] Compare Guertler and Tammann, *Zeit. anorg. Chem.*, 1905, **47**, 163; Vigouroux, *Compt. rend.*, 1905, **141**, 828; Vanzetti, *Gazz.*, 1906, **36**, i, 498.

[7] See *Zeit. Nahr. Genussm.*, 1906, **12**, 132; *J. Soc. Chem. Ind.*, 1907, **26**, 968; 1909, **28**, 25, 143; 1910, **29**, 154, 280, 355, 955; *Stahl und Eisen*, 1912, **32**, 267.

Silicates of Iron.—Several ferrous and ferric silicates occur in the mineral kingdom, but they are more frequently found as double silicates, in which the alkali metals and the metals of the alkaline earths are present. These are generally isomorphous mixtures in which ferric oxide is replaced by alumina, whilst lime, magnesia, and the alkalis are substituted by ferrous oxide, manganous oxide, &c. For a description of these compounds works on mineralogy must be consulted.

The Iron Tree.—In Glauber's description of the preparation of *oleum martis* (see p. 1228) the following passage occurs:—"When such a red *massa* before it deliquesces to an *oleum* is laid in *oleum arenæ vel silicum* (the modern sodium silicate) for one or two hours, a tree grows out of it, with roots, stems, many branches, and twigs, wonderful to behold." This phenomenon depends upon the fact that water-glass, which always contains some carbonate, decomposes the ferric chloride into ferric silicate and basic ferric carbonate, whilst bubbles of carbon dioxide are given off, and thus filiform processes are produced. In place of the ferric chloride, ferrous chloride, cobalt chloride, nickel chloride, copper nitrate, and many other easily soluble metallic salts may be employed, and thus a series of differently coloured coral-like growths may be produced.

Detection and Estimation of Iron.

582 The ferrous salts, as has been stated, readily absorb oxygen, and their solutions, therefore, usually contain larger or smaller quantities of the ferric salts. Hence they give a bluish-white precipitate with ferrocyanide of potassium, and this on shaking with air assumes a dark-blue colour. Ferricyanide of potassium produces at once a dark-blue precipitate, whilst the ferric salts are coloured dark-brown by this reagent, no precipitate being formed. By these reactions it is easy to ascertain whether a ferrous or a ferric salt, or a mixture of both, is contained in a solution.

With alkalis, ferrous salts give a white, or usually greenish precipitate, which quickly changes to a dark-green colour on exposure to air, and afterwards becomes brown. Ferric salts give at once a brown precipitate. The presence of these latter may also be readily ascertained by the blood-red colour which they produce with soluble thiocyanates. A bead of microcosmic salt or borax is coloured dark-green by ferrous salts. This

colour readily changes to a yellow or reddish-brown by oxidation. On cooling, the colour becomes less distinct, disappearing altogether if only traces of ferric oxide are present. Iron can also be detected in the dry way by Bunsen's test. For this purpose the compound is heated on the end of a carbonised wooden match, which has previously been impregnated with fused sodium carbonate, held in the reduction zone of the non-luminous gas flame. The whole is then rubbed up in an agate mortar with a little water, the particles of iron being extracted on the point of a magnetised knife-blade. The adhering particles of finely divided iron are brought on to a small piece of filter paper, dissolved in a drop of aqua regia and a drop of potassium ferrocyanide added, this confirmatory test being necessary inasmuch as nickel and cobalt are also magnetic metals.

It has been stated already that manganese is obtained together with iron in the course of qualitative analysis and the mode of their separation has been described. The precipitate containing ferric hydroxide may also contain uranium. This is readily separated by digesting the precipitate with a concentrated solution of ammonium carbonate. The washed residue is then dissolved in hydrochloric acid and the confirmatory test for iron applied.

The iron compounds do not impart any colour to the non-luminous gas flame. The spectrum of the metal is extraordinarily rich in lines, more than 4,500 having been measured. A dark line in the solar spectrum corresponds to each of the bright lines in the visible part of the spectrum.

In the processes of *quantitative analysis* iron is estimated both gravimetrically and volumetrically. In the first case the iron must be present as ferric salt. Ferrous salts are, therefore, previously oxidised with nitric acid and then precipitated with ammonia, the precipitate washed with boiling water, dried, ignited, and weighed as the sesquioxide. If the solution should contain tartaric acid, sugar, or other organic compounds, ammonia produces no precipitate. In these cases the iron must be previously precipitated as sulphide; this is well washed with water containing ammonium sulphide, dissolved in nitric acid and the iron precipitated with ammonia, or the organic compound may be destroyed by ignition. If other metals precipitable by ammonia and ammonium sulphide are present, the iron can be separated by adding sodium or ammonium

formate, acetate, or succinate to the neutral solution and boiling, when basic ferric formate, acetate, or succinate is thrown down. This is filtered whilst hot, washed with boiling water, dried, ignited, and weighed as ferric oxide. The precipitate may contain alumina, and this must then be separated by means of caustic potash. For the separation of iron from various other metals the use of nitrosophenylhydroxylamine, known as "cupferron," has been proposed.[1]

The chief *volumetric* processes for the estimation of iron depend upon the amount of oxygen required to convert it from the ferrous into the ferric form, and the solutions to be tested must first have the iron completely reduced to the ferrous state. For this purpose many reducing agents may be employed, the methods most frequently used being (1) treatment with zinc or aluminium in acid solution, (2) treatment with sulphuretted hydrogen, (3) boiling with ammonium bisulphite solution, and (4) addition of stannous chloride to the boiling solution. In the case of (2) and (3) the excess of reducing agent is removed by boiling, and in (4) the excess of stannous chloride is precipitated by addition of mercuric chloride.

The oxidising medium employed is a standard solution of potassium permanganate or dichromate, these being standardised by means of pure iron wire, recrystallised oxalic acid, or pure ferrous ammonium sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, the latter containing exactly one-seventh of its weight of iron. In carrying out the permanganate method, the ferrous solution prepared as above described is acidified with sulphuric acid and titrated with the permanganate solution until a permanent pink coloration is produced. Permanganate cannot, however, be used without special precautions when hydrochloric acid is present, and in that case it is better to employ dichromate, which may also be used in presence of sulphuric acid. The completion of the reaction is ascertained in this case by bringing a drop of the solution in contact with a very dilute freshly prepared solution of potassium ferricyanide, free from ferrocyanide, on a white porcelain plate; the dichromate is added until no blue coloration is obtained.

Methods have also been proposed for the direct volumetric estimation of ferric iron, without a preliminary reduction to the ferrous state. The reducing agent chiefly employed for this

[1] Baudisch, *Chem. Zeit.*, 1909, **33**, 1298; Biltz and Hödtke, *Zeit. anorg. Chem.*, 1910, **66**, 426; Fresenius, *Zeit. anal. Chem.*, 1911, **50**, 35.

purpose, in the form of a standard solution, is titanium trichloride (p. 815), potassium thiocyanate being added as indicator to the acidified solution of the ferric salt. The titration is carried out in an atmosphere free from oxygen, and the addition of titanium trichloride is continued until the red colour due to ferric thiocyanate has disappeared entirely.[1]

The *Atomic Weight* of iron has been accurately determined by several chemists. Svanberg and Norlin,[2] by reducing the oxide in hydrogen, obtained the number 56·09; Berzelius found 56·05 by oxidising the metal with nitric acid, and Erdmann and Marchand,[3] who reduced the oxide in hydrogen, obtained 56·02. Maumené,[4] dissolving pure iron wire in nitric acid and precipitating with ammonia, found the number 56·00; and Dumas,[5] by the analysis of ferric chloride, obtained 56·23, whilst the analysis of ferrous chloride gave 56·09. By the reduction of ferric oxide, obtained from carefully purified ferric nitrate, with hydrogen, Richards and Baxter obtained the value 55·88 and from the amount of silver bromide yielded by ferrous bromide, the number 55·85.[6] The value at present (1913) adopted is 55·84.

COBALT. Co = 58·97.

583 The word cobalt occurs in the writings of Paracelsus and Agricola as well as in those of "Basil Valentine"; two meanings were attached to this name; in the first place it signified a sprite or goblin supposed to haunt the mine, whilst in the second place it was used to denote certain minerals, which are too imperfectly described for exact identification. It appears, however, that in this latter sense it was employed to designate minerals which, although they possessed the appearance of a well-known metallic ore, did not yield any of this metal when subjected to the usual treatment. Hence the word came to

[1] See Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis* (Longmans, 1910).

[2] *Annalen*, 1844, **50**, 432.

[3] *Annalen*, 1844, **52**, 212.

[4] *Ann. Chim. Phys.*, 1850, [3], **30**, 380.

[5] *Ann. Chim. Phys.*, 1859, [3], **55**, 157.

[6] *Zeit. anorg. Chem.*, 1900, **23**, 245; 1904, **38**, 232. Compare Baxter and others, *J. Amer. Chem. Soc.*, 1911, **33**, 319, 337; 1912, **34**, 1657.

signify a false ore. In later times the same name was given to the mineral which was used for the purpose of colouring glass blue, and is still employed for the preparation of smalt. In 1735, Brandt stated that the blue colour of smalt depends upon the presence of a peculiar metal to which he gave the name kobalt-rex, and in 1742 he showed that the colour of smalt does not depend, as had been believed, upon the presence of arsenic and iron, metals which are usually found in cobalt ores, for he found that some of these ores occur free from arsenic, and that these likewise give the blue colour. The new metal was stated to be magnetic and extremely infusible. These observations were confirmed by Bergman in 1780, and the compounds of cobalt were afterwards examined by many chemists.

Cobalt does not occur in the free state in nature, and its ores, which usually contain nickel, are not very widely distributed. It is found as linnaeite, $(Co,Ni,Fe)_3S_4$; skutterudite, $CoAs_3$; speiss-cobalt or smaltite, $(Co,Ni,Fe)As_2$; cobaltite or cobalt glance, (Co,Fe)AsS; earthy cobalt, or wad, $(Co,Mn)O,2MnO_2,4H_2O$; erythrite, or cobalt bloom, $Co_3,AsO_4)_2,8H_2O$, &c.

The bulk of the cobalt of commerce is obtained from the district surrounding Cobalt city, in Ontario, where there are rich silver ores containing a notable proportion of cobalt and nickel, chiefly as arsenides. Deposits of oxides and sulphides of cobalt and nickel occur also in New Caledonia. Cobalt is almost always found as a constituent of meteoric iron, and its presence has been detected in the solar atmosphere.

Treatment of Cobalt Ores.—For the preparation of cobalt compounds speiss-cobalt or other arsenical ores are employed. These, after roasting or calcination in the air, yield an impure cobalt arsenate which comes into commerce under the name of *zaffre*, and which is further worked up as hereafter described. The cobalt ores, however, mostly contain large quantities of nickel and iron as well as other metals, and for this reason they are usually smelted in order to get rid of the greater part of the iron, the process employed being similar to that which is used for the extraction of copper. The roasted ore is fused with a flux of calcium carbonate or sand, when the iron slag flows on to the surface while the cobalt remains below as a heavy *speiss* or stone. The roasted ore or the speiss is then dissolved in strong hydrochloric acid, any arsenate of iron which may be present being precipitated by the careful addition of bleaching

powder solution and a small quantity of milk of lime; the clear supernatant liquid is drawn off, treated with sulphuretted hydrogen for the purpose of separating copper, bismuth, &c., and the oxide of cobalt is then precipitated from the clarified solution by bleaching powder. The oxide thus obtained is washed and ignited, and this is brought into the market and largely used for colouring glass and porcelain, as well as for the preparation of the chloride and nitrate of cobalt. This oxide usually contains iron, and almost always nickel and other impurities.

In the case of the New Caledonia ores, consisting chiefly of sulphides, the cobalt, nickel, &c., are converted into sulphates either by careful calcination at a moderate temperature, or by treatment with ferrous sulphate solution. The cobalt is then separated from the other metals which form soluble sulphates, and is finally obtained as oxide.

A small amount of cobalt is extracted in the form of oxide by the treatment of ores and metallurgical products containing nickel by a wet method. These materials are roasted sweet (*i.e.* free from sulphur and arsenic), and the oxides thus formed dissolved in hydrochloric or sulphuric acid. The solution is then treated as described above for the separation of iron, the metals which are precipitated by sulphuretted hydrogen, and cobalt. The liquid resulting from the separation of the cobalt is further treated with milk of lime for the separation of nickel hydroxide, which is afterwards reduced to metal.[1]

584 *Preparation of Metallic Cobalt.*—This metal is obtained as a grey powder by igniting the oxide or chloride in a current of dry hydrogen, or by reduction of the oxide with charcoal or aluminium. By strongly heating the oxalate under a layer of powdered glass the metal can be obtained as a coherent mass, and this may be fused to a regulus by heating it in a crucible made of lime, magnesia, or graphite.

Pure cobalt may be obtained, according to Winkler,[2] by electrolysing a solution of pure cobalt sulphate in presence of ammonium sulphate and ammonia, platinum electrodes being used. The metal thus deposited invariably contains a small amount of oxygen (0·2—0·3 per cent.), and must therefore be heated in pure hydrogen. Pure metallic cobalt may be obtained

[1] For other methods of treating cobalt ores see Pedersen, *Metallurgie*, 1911, **8**, 335; Barth, *ibid.*, 1912, **9**, 199.

[2] *Zeit. anorg. Chem.*, 1895, **8**, 1.

also by heating cobalt carbonyl (see p. 1292) to a suitable temperature.[1]

Cobalt possesses the colour of polished iron; it is, however, harder than this metal. It melts at 1490°,[2] and may be distilled in the electric furnace.[3] It is malleable and very tough; it is magnetic up to 1150°, and has a specific gravity of 8·8 at 15°.[4] Cobalt in the form of powder absorbs oxygen from the air, often with ignition; the compact metal, however, does not undergo change at the ordinary temperature, but slowly oxidises when heated, and at a very high temperature burns with a red flame. The metal also burns at 150° in nitric oxide, forming the monoxide.[5] It is capable of absorbing 59–153 volumes of hydrogen. The metal is readily soluble in hydrochloric, dilute sulphuric, and nitric acids, and decomposes steam at a red heat. It may exist in the passive state, but exhibits this property to a less extent than nickel.[6]

Cobalt combines with boron to form a crystalline compound which resembles the corresponding nickel compound, and is obtained in a similar manner.[7]

The character of the alloys which cobalt forms with other metals has been investigated by the method of thermal analysis, controlled by microscopic observations.[8]

Nickel and cobalt separate from their fused mixtures in mixed crystals, the composition of which is approximately that of the liquid from which they are deposited.[9]

[1] Eng. Patent 13207; 20/6/1908.

[2] Day and Sosman, *Amer. J. Sci.*, 1910, **29**, 161.

[3] Moissan, *Annalen*, 1906, **351**, 510.

[4] Copaux, *Compt. rend.*, 1905, **140**, 657.

[5] Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429.

[6] Hittorf, *Zeit. physikal. Chem.*, 1900, **34**, 385; Byers, *J. Amer. Chem. Soc.* 1908, **30**, 1718.

[7] See du Jassonneix, *Compt. rend.*, 1907, **145**, 240.

[8] See Sahmen, *Zeit. anorg. Chem.*, 1908, **57**, 1; Gwyer, *ibid.*, 113; Lewkonja, *ibid.*, **59**, 293.

[9] Guertler and Tammann, *Zeit. anorg. Chem.*, 1904, **42**, 353; Ruer and Kaneko, *Metallurgie*, 1912, **9**, 422.

COMPOUNDS OF COBALT.

Cobalt and Oxygen.

585 Cobalt forms three well-defined oxides:

Cobalt monoxide, CoO,
Cobalt sesquioxide, Co_2O_3,
Tricobalt tetroxide, Co_3O_4.

In addition to these the dioxide, CoO_2, probably exists, and several others such as Co_8O_9,[1] Co_6O_7,[2] Co_4O_5,[3] and Co_3O_5[4] have been described.[5]

Of these oxides, the first, CoO, is a well-marked basic oxide, corresponding to the stable cobaltous salts in which the metal is divalent. The sesquioxide acts as a feebly basic oxide: the corresponding salts are unstable and are easily reduced to cobaltous salts. The dioxide appears to have a decided acidic function, and several stable cobaltites are known.

Cobalt Monoxide or Cobaltous Oxide, CoO.—This compound is obtained by reducing the higher oxide by heating it either in a current of hydrogen to a temperature not above 350° (Winkelblech), or in a current of carbon dioxide to redness until its weight is constant (Russell).[6] It is a light-brown powder, which does not alter in the air at the ordinary temperature, but when heated yields tricobalt tetroxide, Co_3O_4. When heated in the electric furnace, it melts and yields rose-coloured needles.

Cobaltous Hydroxide, $Co(OH)_2$, is obtained by precipitating a cobaltous salt with caustic potash in the absence of air. A blue basic salt is first obtained, and this, on boiling, is quickly converted into a rose-red coloured hydroxide.[7] It absorbs oxygen from the air, the colour changing to brown, and dissolves in hot very concentrated potash, crystallising out on cooling in microscopic prisms.[8]

[1] *Zeit. anal. Chem.*, 1868, **7**, 336; *J. pr. Chem.*, 1856, **69**, 131.
[2] *Pogg. Ann.*, 1844, **61**, 472; 1851, **84**, 560.
[3] *Jahresber.*, 1868, 265. [4] *Journ. Chem. Soc.*, 1890, **58**, 1213.
[5] See also Taylor, *Mem. Manch. Phil. Soc.*, 1903, [5], **12**, 1.
[6] *Journ. Chem. Soc.*, 1863, **16**, 51.
[7] See Hantzsch, *Zeit. anorg. Chem.*, 1912, **73**, 304.
[8] de Schulten, *Compt. rend.*, 1889, **109**, 266; compare Job, *ibid.*, 1907, **144**, 1044.

The cobaltous salts may be prepared by the action of acids on cobaltous hydroxide. They are the most stable of the cobalt salts, but undergo oxidation more readily than the corresponding compounds of nickel. In the anhydrous state they possess a deep violet or blue colour, and in the hydrated condition a rose-red tint.

Cobaltic Oxide or Cobalt Sesquioxide, Co_2O_3, is a dark-brown powder, formed by gently igniting the nitrate.

Cobaltic Hydroxide, $Co(OH)_3$, is prepared by precipitating a cobalt salt with an alkaline hypochlorite solution. The composition of this precipitate depends on the conditions under which it has been produced, and frequently, especially when prepared in the cold, it contains more oxygen than corresponds to the formula Co_2O_3.[1] The sesquioxide is also obtained in a hydrated condition when an alkaline solution of cobalt sulphate is electrolysed,[2] or when a solution of the same salt is treated with potassium or ammonium persulphate.[3] It forms a brownish-black powder, which is decomposed by hydrochloric acid with evolution of chlorine, and by oxy-acids with evolution of oxygen.

The sesquioxide and its hydroxide act, therefore, as peroxides, but at the same time they possess weak basic properties, inasmuch as they dissolve in well-cooled acids forming brownish-yellow solutions. One of the most stable of these compounds is a strongly coloured solution obtained by dissolving the hydroxide in acetic acid; this decomposes only when heated. The corresponding sulphate and some of its double salts have however been isolated in the crystalline form.

Tricobalt Tetroxide or Cobalto-Cobaltic Oxide, Co_3O_4.—This compound, which corresponds to the magnetic oxide of iron, is formed when one of the other oxides or the nitrate is heated in the air; thus obtained, it forms a black powder having a specific gravity of about 6·0. If a dry mixture of sal-ammoniac and cobalt oxalate or cobalt chloride be heated in the air, or in oxygen, this compound is obtained in hard, microscopic octahedra, which have a metallic lustre, and are not magnetic. It is obtained in the hydrated state by the oxidation of moist cobaltous hydroxide in the air and also by warming cobaltous hydroxide with excess of potassium persulphate, washing and

[1] Carnot, *Compt. rend.*, 1889, **108**, 610; Schröder, *Journ. Chem. Soc.*, 1890, **58**, 1213; Hüttner, *Zeit. anorg. Chem.*, 1901, **27**, 81.

[2] Coehn and Gläser, *Zeit. anorg. Chem.*, 1903, **33**, 9.

[3] Mawrow, *Zeit. anorg. Chem.*, 1900, **24**, 263; Hüttner, *loc. cit.*

heating the product at 100° with dilute nitric acid.[1] When heated in the oxy-coal-gas flame it yields metallic cobalt, which becomes covered with a film of oxide as it cools.[2] The substance obtained by fusing one of the oxides with caustic potash, which was thought to be a potassium cobaltite,[3] $Co_9O_{16}K_2,3H_2O$, is probably cobalto-cobaltic oxide contaminated with potash,[4] or cobaltous potassium cobaltite.[5]

Cobalt Dioxide, CoO_2, has not been obtained in the pure state. It appears, however, to be formed as a greenish-black precipitate when iodine and caustic soda are added to a solution of a cobaltous salt.[6] An oxide approaching this in composition is also formed by the action of a hypochlorite on a cobaltous salt, and is probably instrumental in bringing about the well-known evolution of oxygen which occurs when bleaching powder solution is warmed with a small quantity of a cobalt salt (Vol. I., p. 245).[7]

According to McConnell and Hanes,[8] when cobaltous hydroxide is suspended in water and treated with hydrogen peroxide, and the liquid filtered, a strongly acid colourless filtrate is obtained which appears to contain cobaltous acid, H_2CoO_3. If potassium bicarbonate be added to this filtrate, or if the oxidation be carried out in presence of potassium bicarbonate, a green solution is obtained, which probably contains potassium cobaltite, K_2CoO_3. On the other hand, Durrant[9] has failed to obtain evidence of the existence of this acid, and considers the green colour to be due to a derivative of cobaltic oxide to which he assigns the formula $[Co(KCO_3)_2]_2O$. Similar green compounds have been obtained with potassium salts of organic carboxylic acids and these may be formulated as derivatives of the radical >Co.O.Co<. Sulphuric and sulphurous acids decolorise the green solution, but the colour reappears on neutralisation with potassium bicarbonate. Acetic acid does not decolorise the liquid, whilst, on warming with sulphuric acid, a pink solution of cobaltous sulphate is obtained.

[1] Mawrow, *loc. cit.* [2] Read, *Journ. Chem. Soc.*, 1894, **65**, 314.

[3] Schwarzenberg, *Annalen*, 1856, **97**, 212; Pebal, *ibid.*, 1856, **100**, 257; Mayer, *ibid.*, 1857, **101**, 266.

[4] McConnell and Hanes, *Journ. Chem. Soc.*, 1897, **71**, 584.

[5] Bellucci and Dominici, *Atti R. Accad. Lincei*, 1907, [v], **16**, i., 315.

[6] Vortmann, *Ber.*, 1891, **24**, 2744.

[7] McLeod, *British Assoc. Reports*, 1892, 669.

[8] *Journ. Chem. Soc.*, 1897, **71**, 584.

[9] *Proc. Chem. Soc.*, 1896, **12**, 96, 244; *Journ. Chem. Soc.*, 1905, **87**, 1781; see also Job, *Compt. rend.*, 1898, **127**, 100.

Barium Cobaltite, BaO,CoO_2, and *Barium Dicobaltite*, $BaO,2CoO_2$, are formed in black crystals when cobalt sesquioxide is fused with baryta and barium chloride.[1] These compounds evolve chlorine when treated with hydrochloric acid.

Magnesium Cobaltite, MgO,CoO_2, is formed as a deep garnet-red mass when magnesia is fused with cobalt sesquioxide in the electric furnace.[2]

Cobaltous Cobaltite, $CoO,2CoO_2,2H_2O$, is obtained by fusing cobaltous oxide with potassium peroxide, washing the cooled mass first with water and then with dilute sulphuric acid, and finally again with water, and drying over phosphoric oxide in a vacuum. It forms six-sided plates, and evolves chlorine when treated with hydrochloric acid.[3]

Cobalt and the Halogens.

586 *Cobaltous Fluoride*, CoF_2, is obtained by dissolving the oxide or carbonate in hydrofluoric acid; on evaporation, rose-red crystals are deposited having the composition $CoF_2,2H_2O$: these are decomposed by boiling water with the formation of a light-red insoluble oxyfluoride.

The anhydrous fluoride is prepared by heating the chloride with ammonium fluoride in a current of hydrogen fluoride, and forms rose-coloured prisms which are slightly soluble in water.[4]

It forms double salts with the alkali fluorides.[5]

Cobaltic Fluoride, CoF_3, is obtained as a green powder when a saturated solution of cobaltous fluoride in 40 per cent. hydrofluoric acid is electrolysed in a platinum dish which acts as anode, a platinum wire being employed as cathode. It is decomposed by water with formation of cobaltic hydroxide.[6]

Cobalt Chloride, $CoCl_2$.—Powdered metallic cobalt takes fire when warmed in chlorine gas, forming blue crystalline scales of the anhydrous chloride, which can be readily sublimed in a current of chlorine. They dissolve in alcohol, forming a blue solution, and on addition of water first become violet, and then rose-coloured. Cobalt chloride is obtained in aqueous solution

[1] Rousseau, *Compt. rend.*, 1889, **109**, 64.

[2] Dufau, *Compt. rend.*, 1896, **123**, 239.

[3] Hofmann and Hiendlmaier, *Ber.*, 1906, **39**, 3186. Compare Bellucci and Dominici, *Atti R. Accad. Lincei*, [v.], 1907, **16**, i., 315.

[4] Poulenc, *Compt. rend.*, 1892, **114**, 1426.

[5] Compare Böhm, *Zeit. anorg. Chem.*, 1905, **43**, 326.

[6] Barbieri and Calzolari, *Atti R. Accad. Lincei*, 1905, [5], **14**, i., 464.

by dissolving the carbonate, or one of the oxides, in hydrochloric acid; short dark-red monoclinic prisms crystallise on cooling the concentrated warm solution; these possess the composition $CoCl_2,6H_2O$, and have a specific gravity of 1·84. When these crystals are allowed to stand over sulphuric acid at 50° the rose-coloured dihydrate, $CoCl_2,2H_2O$, is formed, and when heated to 100° the deep-violet monohydrate remains, which at 110—120° yields the blue anhydrous chloride. A hydrate with $4H_2O$ has also been obtained.[1] A strong aqueous solution is rose-coloured, but becomes blue when it is heated, and when concentrated hydrochloric or sulphuric acid or alcohol is added. The rose colour is restored when the chloride of zinc, mercury, antimony, or tin is added to the solution which has been rendered blue by hydrochloric acid. These changes of colour have been attributed by some to the formation and decomposition of double salts or complex ions, by others to the hydration and dehydration of the cobalt salt.[2]

An unstable compound, $CoCl_2,HCl,3H_2O$, separates in blue crystals at $-23°$ from a saturated solution of cobalt chloride in hydrochloric acid. A corresponding lithium compound is known which is also blue.[3]

When anhydrous cobalt chloride is treated with ammonia the compound $CoCl_2,6NH_3$ is formed.[4]

Sympathetic Inks.—If a dilute solution of the chloride be used as an ink the writing is not visible when it is allowed to dry in the air, but on warming, the characters appear of a bright blue colour, disappearing again gradually on standing in the air, owing to the absorption of moisture.

From this property the cobalt salts have been employed for the manufacture of the so-called *sympathetic inks*; by this is understood any liquid the writing of which is invisible under ordinary conditions but can be rendered apparent by some simple treatment. The first attempt at the preparation of such an ink depended upon the fact that a solution of lead

[1] de Coninck, *Bull. Acad. roy. Belg.*, 1904, 1170.

[2] See Engel, *Bull. Soc. chim.*, 1891, **6**, 239; Potilitzine, *ibid.*, 264; Etard, *Compt. rend.*, 1891, **113**, 699; Charpy, *ibid.*, 794; Sabatier, *ibid.*, 1888, **107**, 42; Donnan and Bassett, *Journ. Chem. Soc.*, 1902, **81**, 939; Hartley, *ibid.*, 1903, **83**, 401; Moore, *Zeit. physikal. Chem.*, 1906, **55**, 641; Lewis, *ibid.*, **56**, 223; Benrath, *Zeit. anorg. Chem.*, 1907, **54**, 328; Denham, *Zeit. physikal. Chem.*, 1909, **65**, 641; Houstoun, *Proc. Roy. Soc. Edin.*, 1911, **31**, 521–558.

[3] Chassevant, *Ann. Chim. Phys.*, 1893, [6], **30**, 5.

[4] Ephraim, *Ber.*, 1912, **45**, 1322.

acetate becomes black when treated with a decoction of orpiment in milk of lime. These two liquids were mentioned by Lemery in 1681 as "encres appellées sympathiques." In the treatise termed *The Key to unlock the Cabinet of the Secrets of Nature*, published in 1705, a method for preparing a sympathetic ink from certain bismuth ores is described. The peculiar properties of this ink were believed to be due to bismuth, but in 1744 Gessner proved that the cobalt in the ores was the active agent in the production of the ink. This property of the cobalt salts to change colour from rose to blue on loss of water has been applied also to the construction of floral hygrometers. Artificial flowers are prepared, the petals of which are tinted with cobalt salts. In damp weather the flower is pink, in dry weather violet or blue. This invention is, we need scarcely add, a Parisian one.

Cobalt Bromide, $CoBr_2$.—If bromine vapour is passed over metallic cobalt at a dark-red heat, a green fused mass is formed which absorbs water from the air, yielding a dark-red liquid. This solution is obtained also by bringing cobalt, bromine, and water together; if the solution is allowed to stand over sulphuric acid, dark-red prisms having the composition $CoBr_2,6H_2O$ are deposited, and these when heated to 100° give a purple mass containing $CoBr_2,2H_2O$, which at 130° yields the anhydrous bromide as an amorphous green mass (Rammelsberg, Hartley).

Cobalt Iodide, CoI_2.—This substance is formed with evolution of heat when finely divided cobalt is gently warmed with water and iodine. The saturated solution is red up to 20°, and then passes through brown and olive to green at 35°. When poured into a saturated solution of magnesium chloride a blue solution is formed (Etard). The hydrate $CoI_2,6H_2O$ is dark-red, whilst the tetrahydrate and the dihydrate are green, and the anhydrous salt resembles iodine. Double salts of this compound with other iodides are known.[1]

Cobalt Chlorate, $Co(ClO_3)_2$, is a somewhat unstable salt, which forms various hydrates.[2]

Cobalt Iodate, $Co(IO_3)_2$, crystallises from water in three forms: as anhydrous salt, as dihydrate, and as tetrahydrate.[3]

[1] Dobroserdoff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 303; Mosnier, *Ann. Chim. Phys.*, 1897, [7], **12**, 374.

[2] Meusser, *Ber.*, 1902, **35**, 1417.

[3] Meusser, *Ber.*, 1901, **34**, 2432.

Cobalt and Sulphur.

587 *Cobalt Monosulphide*, CoS, is obtained as a black hydrated precipitate when a solution of a cobalt salt is mixed with ammonium sulphide. It dissolves in concentrated hydrochloric acid with evolution of sulphuretted hydrogen. The cold dilute acid dissolves it but slowly, whilst it is almost insoluble in dilute acetic acid. When the monosulphide is mixed with sulphur and the mixture ignited in a current of hydrogen the following sulphides are formed according to the temperature employed: CoS_2, Co_2S_3, CoS; and at a white heat, Co_2S (H. Rose). The monosulphide is found as an Indian mineral known as syepoorite, occurring in ancient schists in grains or veins of a yellowish steel-grey colour.

Investigation of the freezing points of mixtures of cobalt and sulphur, containing up to 33·6 per cent. of the latter element, indicates the existence of the compounds Co_4S_3 and CoS.[1]

Cobalt pyrites or linnaeite, $(Co,Ni,Fe)_3S_4$, occurs at Bastnäs, near Riddarhyttan, at Müssen in Prussia, as well as at Mineral Hill in Maryland, and at Mine La Motte in Missouri. It forms steel-grey or tarnished copper-red regular octahedra, and occurs also in the massive state. It usually contains more or less nickel, as well as some iron and copper. The same compound can be obtained artificially as a blackish-grey powder by heating a solution of a cobalt salt with potassium polysulphide to a temperature of 160°.

A *Polysulphide of Cobalt*, which probably has the formula Co_2S_7, is obtained as a black precipitate when a solution of sodium monosulphide saturated with sulphur is added to one of cobalt chloride at the ordinary temperature.[2]

Cobaltous Sulphite, $CoSO_3,5H_2O$, is a pink crystalline powder.

Cobaltic Sulphite has not been isolated, but several double compounds, which are probably salts of a complex cobaltisulphurous acid, $H_3[Co(SO_3)_3]$, have been described.[3]

Cobaltous Sulphate, $CoSO_4,7H_2O$.—This salt occurs native as cobalt vitriol, or bieberite, in crystalline crusts. It is prepared

[1] Friedrich, *Metallurgie*, 1908, **5**, 212. Compare Bellucci, *Atti R. Accad. Lincei*, 1908, [v], **17**, i., 18.

[2] Chesneau, *Compt. rend.*, 1896, **123**, 1068.

[3] Berglund, *Ber.*, 1874, **7**, 469.

artificially by dissolving the carbonate or oxide in dilute sulphuric acid, and crystallises in red prisms having the form of iron vitriol, which are unalterable in the air. It has a specific gravity of 1·924 (Schiff), possesses a weak astringent metallic taste, is easily soluble in water, but does not dissolve in alcohol. According to Mulder 100 parts of water dissolve:

At	0°	10°	20°	30°	50°	70°	100°
$CoSO_4$	24·6	29·5	34·5	40·2	51·8	63·8	82·6.

When its solution is allowed to stand at 40°–50° monoclinic crystals having the composition $CoSO_4,6H_2O$ are formed, and these are isomorphous with the corresponding zinc salt. If a concentrated solution of cobalt sulphate is poured gently into sulphuric acid a peach blossom coloured powder, $CoSO_4,4H_2O$, is deposited. The hydrate $CoSO_4,H_2O$ is deposited when a solution of the salt is made slightly acid with sulphuric acid and evaporated.[1] All the hydrates lose their water on heating, but do not fuse, becoming opaque and of a rose-red colour (Proust). Cobalt sulphate forms numerous double salts. It has the power of absorbing notable quantities of nitric oxide, although the absorption is not accompanied by any change of colour.[2] It combines also with ammonia.[3]

Cobaltic Sulphate, $Co_2(SO_4)_3,18H_2O$, is deposited in blue, silky needles, when a cooled acid solution of cobaltous sulphate is electrolysed in a divided cell. It dissolves in water, forming a blue solution which rapidly decomposes with evolution of oxygen. The crystals decompose on exposure to the air, finally becoming pink. It forms a greenish-blue solution in dilute sulphuric acid, which gives a black precipitate with alkalis and is rapidly decomposed by reducing agents. Hydrochloric acid decomposes the salt with evolution of chlorine.[4]

Cobaltic Ammonium Alum, $(NH_4)_2SO_4,Co_2(SO_4)_3,24H_2O$, is obtained by adding ammonium sulphate to an acid solution of cobaltous sulphate and passing a weak current. It forms blue octahedra and is stable when dry, but decomposes in solution, ozonised oxygen being liberated. The potassium, rubidium, and cæsium alums have been obtained in a similar manner.[5]

[1] Lescœur, *Ann. Chim. Phys.*, 1895, [7], **4**, 213.
[2] Hüfner, *Zeit. physikal. Chem.*, 1907 **59**, 416.
[3] Ephraim, *Ber.*, 1912, **45**, 1322.
[4] Marshall, *Journ. Chem. Soc.*, 1891, **59**, 760.
[5] Marshall, *loc. cit.* ; Howe and O'Neal, *J. Amer. Chem. Soc.*, 1898, **20**, 759.

Cobalt and Nitrogen.

588 *Cobalt Nitride*, Co_2N, is obtained as a dull-grey powder [1] when metallic cobalt is heated in ammonia at about 470°. It is soluble in hydrochloric and sulphuric acids, and loses its nitrogen when heated to 600°.

Cobalt Azoimide, $Co(N_3)_2$, together with a *basic azoimide*, $N_3Co(OH)$, have been prepared by the action of aqueous azoimide on a cobalt salt, as explosive violet powders.[2]

Nitro-cobalt, $Co_2(NO_2)$, is formed when diluted nitrogen peroxide is passed over reduced metallic cobalt. It is a black mass, which is vigorously decomposed by water, and explodes when mixed with combustible matter.[3]

Cobalt Nitrite.—Neither cobaltous nor cobaltic nitrite has been prepared in the solid state.[4] The double potassium salt described below differs in many of its properties from an ordinary nitrite, and is probably, like the cobalticyanides and the cobaltammine salts, a derivative of a complex acid containing cobalt.[5]

Potassium Cobaltinitrite, $K_3[Co(NO_2)_6]$, which is known as Fischer's salt after its discoverer,[6] is obtained as a yellow precipitate when the solution of a cobaltous salt, acidified with acetic acid, is mixed with a solution of potassium nitrite :

$$CoCl_2+5KNO_2+2HNO_2=K_3Co(NO_2)_6+2KCl+NO+H_2O.$$

As this salt is somewhat soluble in water, it is best to wash it with a solution of potassium acetate, and then with 80 per cent. alcohol. Cobalt yellow, as this compound is also termed, is a bright-yellow powder consisting of microscopic pyramids, or of four- or six-sided stellated forms. According to Sadtler [7] the salt is usually anhydrous; it can, however, be obtained, according to the concentration of the solution, with from one to four molecules of water, and its colour then varies from a bright yellow to a dark greenish-yellow. It is decom-

[1] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1251.
[2] Curtius and Rissom, *J. pr. Chem.*, 1898, [2], **58**, 261.
[3] Sabatier and Senderens, *Bull. Soc. chim.*, 1893, [3], **9**, 669.
[4] See Suzuki, *Journ. Chem. Soc.*, 1910, **97**, 726.
[5] Hofmann and Burger, *Ber.*, 1907, **40**, 3298; Rosenheim and Garfunkel, *ibid.*, 1911, **44**, 1865.
[6] *Pogg. Ann.*, 1848, **74**, 124.
[7] *Amer. J. Sci.*, [2], 1870, **49**, 189.

posed by nitric and hydrochloric acids, but only when heated. Caustic potash solution attacks it with difficulty. Caustic soda or baryta water, on the other hand, decomposes it readily, on gently warming, with precipitation of the brown hydroxide. The salt suspended in water is only slowly attacked by sulphuretted hydrogen, but ammonium sulphide instantly precipitates black cobalt sulphide. The fact that cobalt is precipitated by a solution of potassium nitrite, acidified with acetic acid, is employed in the analytical separation of cobalt from nickel and other metals.[1]

The cobaltinitrites of ammonium, sodium, silver, thallium, and lead are also known, and a solution of the sodium compound is used in testing for potassium.[2] The corresponding compounds of rubidium and cæsium are distinguished by being only one-tenth as soluble as their platinichlorides.[3]

$Rb_3[Co(NO_2)_6],H_2O$ dissolves in 19,800 parts of water.
$Cs_3[Co(NO_2)_6],H_2O$ „ 20,100 „

If a solution of cobalt chloride be precipitated with potassium nitrite without addition of acid, a yellow hydrated precipitate of potassium cobaltous nitrite, $2KNO_2,Co(NO_2)_2$, is obtained, soluble in hot water and yielding a red solution.[4]

Cobalt Nitrate, $Co(NO_3)_2,6H_2O$.—This substance generally forms an indistinctly pink crystalline mass; it may be obtained by slow evaporation in monoclinic prisms, having a specific gravity of 1·83 and not undergoing change in dry air. It begins to melt below 100°, and when more strongly heated the violet liquid becomes thick and green; then it begins to boil, giving off nitrous fumes, and the black oxide is left. Anhydrous cobalt nitrate is a slightly pink powder, which begins to decompose at 100–105°.[5] Hydrates with nine and three molecules of water also exist.[6]

[1] See p. 1317, and Funk, *Zeit. anal. Chem.*, 1907, **46**, 1.

[2] See Adie and Wood, *Journ. Chem. Soc.*, 1900, **77**, 1076; Bülmann, *Zeit. anal. Chem.*, 1900, **39**, 284; Cunningham and Perkin, *Journ. Chem. Soc.*, 1909, **95**, 1562; Burgess and Kamm, *J. Amer. Chem. Soc.*, 1912, **34**, 652.

[3] Rosenbladt, *Ber.*, 1886, **19**, 2531.

[4] Erdmann, *J. pr. Chem.*, 1866, **97**, 385.

[5] Guntz and Martin, *Bull. Soc. chim.*, 1909, [iv], **5**, 1004.

[6] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 407.

Ammoniacal Cobalt Compounds or Cobaltammine Salts.

589 In 1799 Tassaert[1] observed that a solution of a cobalt salt in ammonia assumes a brown colour on exposure to the air, and that this changes on boiling to a wine-red, whilst Thénard,[2] in 1802, stated that these changes were brought about by an absorption of oxygen. This latter observation was confirmed by Proust, who found that, on evaporating the solution, black cobaltic oxide separates out. The compounds which are thus formed have attracted the attention of many chemists,[3] and a very large number of these cobaltammine salts have been prepared, as well as compounds with organic substituted ammonias such as pyridine, quinoline, ethylene diamine, &c. A general account of this class of substances has been given on p. 1051, and only one or two typical compounds of each class are here described.

(1) *Hexammine Salts* (*Luteo-salts*), $[(NH_3)_6Co]X_3$, where X is a univalent acid radical, are formed when dilute solutions of cobaltous salts, containing a large amount of ammonia and ammonium chloride, are exposed to the oxidising action of the air; they are produced also by the action of ammonia on many of the salts containing five molecules of ammonia.

The compound *Hexammine-cobaltic Chloride* (*Luteocobaltic Chloride*), $[(NH_3)_6Co]Cl_3$, is obtained when an ammoniacal cobalt chloride solution is allowed to stand for some time, especially in the presence of sal-ammoniac. The formation of the salt is facilitated by the addition of oxidising substances such as lead dioxide, bromine, &c. (Braun, Mills). It crystallises in reddish-yellow monoclinic prisms or pyramids, which dissolve slowly in cold but readily in hot water. It forms a sparingly soluble platinichloride.

(2) *Pentammine Salts* form two distinct classes of compounds, the *aquo-pentammine salts* (*roseo-salts*), $[H_2O(NH_3)_5Co]X_3$, and the *acido-pentammine salts*, $[X(NH_3)_5Co]X_2$. The latter salts have been distinguished by different names according to the nature of the acid group in the complex radical, the salts of the various series usually possessing characteristic colours.

[1] *Ann. Chim.*, 1798, **28**, 95. [2] *Ann. Chim.*, 1802, **42**, 210.

[3] A history of these compounds will be found in *Untersuchungen der Ammoniakalische Kobalt Verbindungen*, by Fr. Rose, Heidelberg, 1871. For more recent work see the references on p. 1290.

The aquopentammine salts, which are pink, lose water when heated with acids, forming derivatives of the second class, whilst the latter are reconverted into aquopentammine salts by boiling or standing with water. By the action of ammonia on the aquopentammine salts the so-called hydroxypentamminecobalt salts are obtained, thus: $[(H_2O)(NH_3)_5Co]X_3+NH_3=[(OH)(NH_3)_5Co]X_2+NH_4X$.

Chloro-pentammine-cobaltic Chloride (*Chloropurpureo-cobaltic Chloride*), $[Cl(NH_3)_5Co]Cl_2$, is obtained by boiling a solution of roseo-cobaltic chloride; it falls as a red precipitate, soluble at 10° in 287 parts of water, and crystallising in tetragonal prisms. With platinichloric acid it forms the salt, $[Cl(NH_3)_5Co]PtCl_6$, which is almost insoluble in cold water, and separates as a brownish-red powder. If the chloride be triturated with strong sulphuric acid a solution of *chloro-pentammine-cobaltic sulphate*, $[Cl(NH_3)_5Co]SO_4$, is formed, and if nitric acid be added to this solution fine red microscopic crystals of *chloro-pentammine-cobaltic nitrate*, $[Cl(NH_3)_5Co](NO_3)_2$, are thrown down, the solution of which is not precipitated by silver nitrate.

(3) *Tetrammine Salts* are analogous to the pentammine salts, but the complex radical contains only four molecules of ammonia and two other groups, which may be water or the hydroxy-group or a univalent acid radical.

Dichloro-tetrammine-cobaltic Chloride (*Praseo-cobaltic Chloride*), $[Cl_2(NH_3)_4Co]Cl,H_2O$, is usually formed together with the other cobaltammine chlorides. It crystallises in small glistening needles which possess an emerald green colour, whence the term praseo is derived. These dissolve in water, yielding a green solution which soon becomes red, and undergoes decomposition on boiling. If fusco-cobaltic chloride, $Co(NH_3)_4Cl_2(OH)$, be warmed with dilute hydrochloric acid a deep-violet solution is obtained, and this on cooling deposits small violet octahedra which possess the same composition as the green salt, and pass into the latter when dissolved in concentrated sulphuric acid, to which hydrochloric acid is gradually added.

Dinitrito-tetrammine-cobaltic Sulphate (*Croceo-cobaltic Sulphate*), $[(NO_2)_2(NH_3)_4Co]_2SO_4$, is formed when a mixture of solutions of cobalt sulphate and potassium nitrite, saturated with ammonia, is exposed to the air. It is deposited in orange-yellow crystals together with green cobaltic hydroxide. The mixture is filtered and the residue dissolved in hot dilute nitric acid, and from this solution the sulphate is obtained on cooling

in the form of yellow tetragonal tablets. Large wine-red crystals are also obtained from dilute solutions. It is slightly soluble in boiling water.

(4) *Triammine compounds* are formed from the tetrammine salts by loss of ammonia. They possess the general formula $[X_3(NH_3)_3Co]$, and are neutral substances acting as non-electrolytes in aqueous solution. *Aquotriammine salts* are also known, with one or more of the acid groups outside the complex radical, which contains one molecule of water for each acid group replaced.

Trinitrito-triammine-cobalt, $[(NO_2)_3(NH_3)_3Co]$, is prepared by acting on cobaltous chloride solution with ammonia and potassium nitrite (Erdmann), and by the action of ammonium nitrite on cobaltous chloride in presence of acetic acid (Gibbs).

Triaquo-triammine-cobaltic Chloride, $[(H_2O)_3(NH_3)_3Co]Cl_3$, is prepared from trinitrito-triammine cobalt by treating first with dilute acetic acid and then with hydrochloric acid at 0° (Werner).

(5) *Diammine salts* have been very slightly investigated.

Potassium Tetranitrito-diammine cobaltite (Erdmann's salt), $[(NO_2)_4(NH_3)_2Co]K$, is obtained by adding ammonium chloride and potassium nitrite to a solution of cobaltous chloride and gently warming. It forms yellow rhombic crystals.

In addition to the classes of compounds already described several series of substances have been prepared which Werner terms multi-nuclear ammoniacal compounds.[1] Examples of these are the *oxycobaltammines*, $\{O_2[Co_2(NH_3)_5]_2\}X_4$, and the series $\{NH[Co(OH)_2(NH_3)_4]_2\}X_4$, and $\{Co[Co(OH)_2(NH_3)_4]_3\}X_6$.

The relations between the various complex cobalt compounds just described have been successfully interpreted by means of Werner's theory of principal and supplementary valencies (see p. 36). The further development of this theory has suggested the possibility of the occurrence of *cis*- and *trans*-isomerism and of optical isomerism—deductions that have been fully verified by the preparation of substances of this description. These deductions are based on the view that the six groups associated with the cobalt atom are arranged round this central atom in the positions corresponding with the angles of an octahedron.[2]

[1] Werner, *Ber.*, 1907, **40**, 66, 2103.

[2] For a summary of Werner's later work, on both the theoretical and practical sides, see *Chemical Society's Annual Reports*, 1911, **8**, 77; also Werner, *Ber.*, 1912, **45**, 121.

Cobalt with Phosphorus, Arsenic, and Antimony.

590 *Phosphides of Cobalt.*—When pieces of phosphorus are thrown on to heated cobalt a bluish-white brittle mass with a metallic lustre is formed. This tarnishes on exposure to air, melts at a lower temperature than cobalt, and contains 6 per cent. of phosphorus. On heating it burns with formation of a dark-blue glass (Pelletier). When cobalt reduced in hydrogen is heated to dark redness in the vapour of phosphorus, a light-grey mass with a metallic lustre is formed, containing 28·4 per cent. of phosphorus (Schrötter), and corresponding nearly to the formula Co_4P_3. A compound, Co_3P_2, is also formed as a black powder by igniting a normal phosphate in a current of hydrogen.

The *phosphide*, Co_2P, is obtained when cobalt formed by reduction of the oxide or oxalate is heated to redness in the vapour of phosphorus trichloride, tribromide or di-iodide,[1] and a substance of this composition is also produced in grey crystals when finely divided cobalt is heated with a copper phosphide in the electric furnace.[2] The existence of this compound is indicated by the occurrence of a maximum on the freezing point curve for mixtures of phosphorus and cobalt.[3] Another compound, Co_2P_3, is obtained as a black metallic mass by heating cobalt chloride at a dull red heat in the vapour of phosphorus.[4]

Cobalt Arsenide, $CoAs_3$, occurs as skutterudite near Modum, in Norway, crystallised in octahedral forms as well as in the massive state. It possesses a colour from tin-white to a pale lead-grey, and usually contains small quantities of iron and sulphur. Smaltite or tin-white cobalt, $CoAs_2$, usually contains varying quantities of iron and nickel, and occurs in tin-white octahedral forms as well as in the massive state in the Erzgebirge. Cobaltite, cobalt glance, or bright white cobalt, $CoAs_2.CoS_2$ or CoAsS, crystallises in the regular system, usually in pyramid octahedra and their combinations, and a portion of the cobalt is generally replaced by iron. It has a silver-white colour inclining to red, and occurs in Sweden, in Westphalia, and in the Bottolack Mine near St. Just in Cornwall. Other arsenides, Co_3As_2, CoAs, and Co_2As_3, have been prepared.[5]

[1] Granger, *Compt. rend.*, 1896, **123**, 176.
[2] Maronneau, *Compt. rend.*, 1900, **130**, 656.
[3] Schemtschuschny and Schepeleff, *Zeit. anorg. Chem.*, 1909, **64**, 245.
[4] Granger, *Compt. rend.*, 1896, **122**, 1484.
[5] Ducelliez, *Compt. rend.*, 1908, **147**, 424.

Cobalt antimonide, CoSb, and *cobalt di-antimonide*, $CoSb_2$, are crystalline powders melting about 1200° and 700° respectively.[1]

Phosphates and Arsenates of Cobalt.—The normal and monohydrogen cobalt salts of the different modifications of phosphoric acid are rose-red or violet-blue insoluble compounds. The di-hydrogen-orthophosphate is easily soluble in water and forms a gummy mass. The arsenates are similar bodies; the normal arsenate, $Co_3(AsO_4)_2,8H_2O$, occurs native as cobalt bloom or erythrite, in violet monoclinic needles isomorphous with vivianite, or in earthy masses. *Zaffre* is an impure basic arsenate obtained by roasting cobalt glance free from iron, or by dissolving the ore in nitric acid and precipitating with soda. It is used for painting on porcelain.

Three insoluble ammoniacal arsenates have been obtained by the action of arsenic acid on solutions of cobalt salts in the presence of ammonia and ammonium salts. These compounds have the formulæ $Co_3(AsO_4)_2,NH_3,7H_2O$, $Co_3(AsO_4)_2,2NH_3,6H_2O$, and $Co_3(AsO_4)_2,3NH_3,5H_2O$, and may be considered as the normal arsenate in which the water of crystallisation is partially replaced by ammonia.[2]

Cobalt and Carbon.

591 *Carbonates of Cobalt.*—The normal salt, $CoCO_3$, is obtained as a bright-red powder, consisting of microscopic rhombohedra, by heating cobalt chloride to 140° with a solution of sodium bicarbonate saturated with carbon dioxide. The salt, $CoCO_3,6H_2O$, is formed by allowing mixed solutions of cobalt nitrate and sodium bicarbonate, saturated with carbon dioxide, to stand at a low temperature until the amorphous precipitate which is first formed becomes crystalline; the dry salt is converted into the anhydrous salt on warming. When a solution of a cobalt salt is precipitated with normal or acid sodium carbonate, bluish or violet basic cobalt carbonates of varying composition are thrown down.[3] Cobalt carbonate forms a pink double salt with potassium carbonate.[4]

Cobalt Tetracarbonyl, $Co_2(CO)_8$, is obtained by heating cobalt in a nickel-steel vessel at about 150° with carbon monoxide

[1] Ducelliez, *Compt. rend.*, 1908, **147**, 1048.
[2] Ducru, *Compt. rend.*, 1900, **131**, 675.
[3] Compare Meigen, *Journ. Chem. Soc.*, 1905, **88**, ii, 454.
[4] See Wood and Jones, *Proc. Camb Phil. Soc.*, 1907, **14**, 171.

under a pressure of not less than 30 atmospheres.[1] In this way fine orange-coloured crystals of cobalt tetracarbonyl are obtained, which are best kept in a sealed glass tube in an atmosphere of hydrogen or carbon monoxide. If left in contact with the air, the substance decomposes, yielding a basic cobalt carbonate. Cobalt tetracarbonyl is insoluble in water, but dissolves more or less in organic solvents, such as carbon disulphide, ether, and alcohol. The double molecular formula, $Co_2(CO)_8$, is established by cryoscopic determinations. The pure crystals melt at 51° without decomposition, but this sets in immediately thereafter. At 60° decomposition is fairly rapid and results in the formation of

Cobalt Tricarbonyl, $Co(CO)_3$.—This compound crystallises from benzene in jet-black crystals, which may be decomposed with bromine water for the purpose of analysis. It is very liable to change in air, and is sparingly soluble in the common solvents.

Cobaltous Cyanide, $Co(CN)_2,3H_2O$, is a reddish precipitate obtained when solutions of potassium cyanide and a cobalt salt are mixed. It dissolves easily in excess of the precipitant, probably forming a solution of potassium cobaltocyanide. If the solution is treated with dilute hydrochloric acid cobaltous cyanide is again precipitated, but if the solution is previously warmed this does not occur, inasmuch as the more stable potassium cobalticyanide is formed (see below).

The cobaltocyanides and cobalticyanides are analogous in composition to the ferro- and ferri-cyanides (p. 1262), and may be regarded as salts of a complex radical containing cobalt.[2] The cobalt is not precipitated by the usual reagents, but the compounds, especially the cobaltocyanides, are not so stable as the corresponding iron compounds.

Potassium Cobaltocyanide, K_4CoCy_6, is a deep amethyst-coloured crystalline powder, which is obtained by dissolving cobaltous cyanide in potassium cyanide at a low temperature and precipitating with alcohol.

Potassium Cobalticyanide, K_3CoCy_6, is formed when an excess of potassium cyanide is added to a solution of a cobalt salt, together with a little acetic acid or hydrochloric acid, and the liquid well boiled:

$$6KCy + 2CoCy_2 + 2HCy = 2K_3CoCy_6 + H_2.$$

[1] Mond, Hirtz, and Cowap, *Journ. Chem. Soc.*, 1910, **97**, 798.
[2] See Descamps, *Ann. Chim. Phys.*, [5], 1881, **24**, 193.

When a solution of potassium cobaltocyanide is rapidly oxidised by atmospheric oxygen, it is converted into the cobalticyanide, and twice as much oxygen is absorbed as is required by the equation:

$$2K_4CoCy_6 + H_2O + O = 2K_3CoCy_6 + 2KOH.$$

At the end of the reaction hydrogen peroxide is found in the solution in an amount corresponding to the whole of the absorbed oxygen. On the other hand, when a solution of the cobaltocyanide is boiled, hydrogen is evolved equal in volume to the oxygen absorbed by the above oxidation. Manchot and Herzog,[1] therefore, consider that the oxidation of potassium cobaltocyanide in solution is effected by the water, the absorbed oxygen uniting with the hydrogen liberated to form hydrogen peroxide.

This salt crystallises in bright yellow crystals isomorphous with potassium ferricyanide.[2] Copper sulphate yields a blue, and silver nitrate a white precipitate, the salts $Cu_3(CoCy_6)_2$ and Ag_3CoCy_6 being formed. *Ferrous cobalticyanide*, $Fe_3(CoCy_6)_2$, is a white precipitate, whilst *cobaltous cobalticyanide*, $Co_3(CoCy_6)_2,14H_2O$, is a pink precipitate which becomes anhydrous and blue when heated to 200°. Cobalticyanides of other metals[3] and also of organic bases[4] have been described. When the copper salt is decomposed by sulphuretted hydrogen *cobalticyanic acid*, H_3CoCy_6, is formed, and this is deposited in colourless silky needles on evaporating the solution. It is deliquescent, has a strongly acid taste and reaction, and is not attacked even by strong nitric acid.

Cobalt and Silicon, Aluminium, and Zinc.

592 *Cobalt Silicides.*—The compound, Co_2Si, is produced when cobalt is heated with silicon in the electric furnace, or at 1200–1300° in silicon tetrachloride vapour, and forms grey metallic crystals of specific gravity 7·28.[5] By heating cobalt in the electric furnace with copper silicide the *monosilicide*, CoSi, is formed, whilst with excess of silicon or a mixture of copper silicide and silicon, the *disilicide*, $CoSi_2$, is obtained.[6]

[1] *Ber.*, 1900, **33**, 1742; see also Moore, *Chem. News*, 1893, **68**, 295.
[2] Gmelin, *Handbuch Org. Chem.*, **1**, 397.
[3] Miller and Mathews, *J. Amer. Chem. Soc.*, 1900, **22**, 62.
[4] Wagener and Tollens, *Ber.*, 1906, **39**, 410.
[5] Vigouroux, *Compt. rend.*, 1895, **121**, 686; 1906, **142**, 635.
[6] Lebeau, *Ann. Chim. Phys.*, 1902, **27**, 271.

Silicates of Cobalt. Smalt.—The silicates of cobalt do not occur as minerals in nature. Although certain specimens of ancient Egyptian glass have been found to be coloured blue by cobalt, the direct application of the ores of cobalt for this purpose appears to date from the sixteenth century. Smalt is a potash glass coloured an intense blue by cobalt oxide. Up to the middle of the 19th century smalt was largely used for colouring starch, paper, &c., but the introduction of artificial ultramarine has done much to diminish the demand for cobalt blue.

For the preparation of smalt, the ore, such as speiss-cobalt or cobalt glance, free as far as possible from iron and sulphur, is first carefully roasted so that the cobalt mainly is oxidised, whilst nickel, iron, copper, and bismuth remain for the most part unaltered, and separate out as an insoluble speiss when the mixture is melted with glass. The roasted ore is then fused with a mixture of quartz sand and potashes, the fusion being effected in large earthen pots, arranged in a furnace similar to that employed for the manufacture of plate glass. The arsenides of nickel and iron sink to the bottom of the pot and the glass is ladled out into cold water. The blue glass is then ground with water to an impalpable powder under granite stones.

Smalt varies in composition according to the differences in the ores, and the proportion of sand and potashes employed. Thus the amount of silica varies between 56 and 70 per cent., that of potash between 12 and 22, and that of cobalt between 6 and 16 per cent. In addition, smalt contains small quantities of alumina, ferric oxide, and frequently also lime, and oxide of lead; the commoner varieties likewise contain oxide of nickel. Smalt has the advantage as a paint over ultramarine that its colour is not destroyed by the action of acids.

Together with smalt, two other pigments containing cobalt must be mentioned, although their composition is undetermined.

Rinmann's Green is obtained either by precipitating a mixture of zinc sulphate and cobalt sulphate with soda and heating the washed precipitate, or by evaporating a solution of cobalt nitrate with oxide of zinc, or zinc nitrate, to dryness, and igniting the residue. A very intensely green-coloured mass is obtained by heating zinc white with roseocobaltic chloride (p. 1288) to a moderate red heat.[1]

Thénard's Blue or *Cobalt Ultramarine.*—When alumina, or a

[1] Compare Hedvall, *Ber.*, 1912, **45**, 2095.

salt of aluminium, is strongly heated with cobalt oxide or one of its salts, a fine blue-coloured product is obtained. This is prepared on the large scale by heating a mixture of alumina with phosphate or arsenate of cobalt, and is used as a paint.

Detection and Estimation of Cobalt.

593 This metal is characterised by its black sulphide, insoluble in acetic and dilute hydrochloric acids, and by the fine blue colour which its compounds impart to the borax bead. If a cobalt compound be reduced on a carbonised match the metal is obtained in shining white magnetic particles; these dissolve in hydrochloric acid forming a rose-red solution, which becomes blue on evaporation.

Cobalt chloride imparts to the non-luminous gas flame an evanescent rose-red colour, but this does not give any characteristic spectrum. The spark spectrum of the chloride contains a large number of bright lines, and the metal also gives a spectrum consisting of a large number of bright lines of which the following in the blue are the most characteristic (Thalén): 4868, 4840, 4815, 4793, 4780.

Cobalt is usually estimated as the oxide, Co_3O_4, which is obtained by strongly heating the monoxide, carbonate, nitrate, &c., in the air. It may also be weighed as metal obtained by the reduction of the nitrate or the chloride in hydrogen; and when it is combined with a volatile acid it may be estimated as the anhydrous sulphate by heating the salt with sulphuric acid. The metal may also be estimated electrolytically. For the separation of cobalt from nickel special methods must be employed (see p. 1316).

The Atomic Weight of cobalt, like that of nickel, has been frequently determined. Among the earlier determinations may be mentioned those of Rothhoff,[1] Schneider,[2] Marignac,[3] Gibbs,[4] Dumas,[5] Russell,[6] Zimmermann,[7] and Winkler.[8] In an investigation by Hempel and Thiele[9] the reduction of tricobalt

[1] *Pogg. Ann.*, 1826, **8**, 185. [2] *Pogg. Ann.*, 1857, **101**, 387.
[3] *Arch. Sci. Phys. Nat.*, 1858, [2], **1**, 373.
[4] *Amer. J. Sci.*, 1858, [2], **25**, 438.
[5] *Ann. Chim. Phys.*, 1859, [3], **55**, 129.
[6] *Journ. Chem. Soc.*, 1863, **16**, 51; *Chem. News*, 1869, **20**, 20.
[7] *Annalen*, 1885, **232**, 324.
[8] *Zeit. anal. Chem.*, 1867, **6**, 22; *Zeit. anorg. Chem.*, 1895, **8**, 1,
[9] *Zeit. anorg. Chem.*, 1896, **11**, 73.

tetroxide gave the number 58·97, and the analysis of the chloride 58·89. Richards and Baxter[1] determined the ratios of cobalt bromide to silver bromide and to silver, and as the mean of a large number of experiments obtained the number 58·99. They determined also the weight of cobalt obtained by the reduction of cobaltous oxide, chloride, and bromide by heating in hydrogen, and obtained numbers between 58·93 and 59·06. More recently, from the ratios of cobalt chloride to silver and to silver chloride, Baxter and Coffin[2] found the number 59·00. The value at present (1913) adopted is 58·97.

The atomic weight of cobalt is higher than that of nickel, although chemical analogies require that cobalt should precede nickel in the periodic system (p. 67). Further investigation into the cause of this anomaly is needed.

NICKEL. Ni = 58·68.

594 The first mention of an ore of this metal is found in the writings of Hiarni in 1694, the name of kupfer-nickel, signifying false copper, being given to it because, whilst possessing the colour of a copper ore, this latter metal could not be extracted from it. In spite of the failure, the ore was long supposed to contain copper, but after the discovery of cobalt many believed that this metal was contained in kupfer-nickel.[3] In 1751 Cronstedt published in the Transactions of the Stockholm Academy an investigation upon an ore which was obtained from the mines of Helsingland. This gave a green vitriol, which imparted a brown and not a blue colour to glass, and yielded a hard brittle metal. In 1754 he stated that a semi-metal occurred most abundantly in kupfer-nickel, and therefore he proposed to give to it the name of nickel. He likewise showed that the speiss formed in the preparation of smalt consisted to a large extent of nickel, and was not, as had been believed, a burnt cobalt which had lost its spirit. Cronstedt's views did not find general acceptance; but in 1774 Bergman's research on nickel made its appearance, and in this he showed that the nickel which Cronstedt had obtained only in the impure state was in reality a new metal.

[1] *Zeit. anorg. Chem.*, 1898, **16**, 362; 1899, **21**, 250; 1899, **22**, 221; compare Winkler, *ibid.*, 1898, **17**, 236.

[2] *Zeit. anorg. Chem.*, 1906, **51**, 171.

[3] See Link, *Phil. Trans.*, 1726, **34**, 192.

Nickel almost always occurs in nature together with cobalt. Its most important ores are niccolite, nickeline, or kupfer-nickel, NiAs, found in the Saxon mines, in Styria, at Leadhills, and in Connecticut; nickel glance, NiAsS; breithauptite, NiSb; millerite or nickel blende, NiS; linnaeite, $(Co,Ni,Fe)_3S_4$; pentlandite, (Ni,Fe)S; nickel ochre or annabergite, $Ni_2(AsO_4)_2$, $8H_2O$; rewdanskite, $(Ni,Fe,Mg)_3Si_2O_7,2H_2O$, &c. Nickel also occurs frequently in magnetic pyrites, that from the Gap Mine in Pennsylvania containing 5·6 per cent., and being worked for nickel; whilst a similar ore, containing about 2·56 per cent. of nickel, and an equal amount of copper, is worked in Ontario, where it is sometimes accompanied by nickeliferous iron pyrites, $(Ni,Fe)S_2$. Similar ores occur also in Oregon. An important source of nickel has been opened out in New Caledonia, where large quantities of a silicate of nickel called garnierite, $2(Ni,Mg)_5Si_4O_{13},3H_2O$, occur.

Nickel is an essential constituent of meteoric iron (p. 1163), its presence in extra-terrestrial matter having been first detected by Proust. It is contained also in the sun's atmosphere.

Metallurgy of Nickel.

595 The method adopted for the extraction of metallic nickel varies according to the nature of the ore to be treated. Formerly nickel was largely obtained as a by-product from the treatment of complex ores of copper, &c., by long and complicated wet and dry processes, but at the present time most of the nickel is obtained from garnierite and nickeliferous pyrrhotite and chalcopyrite.[1]

The method of treating garnierite, as at present practised, consists in smelting the ore with the addition of calcium sulphate or even alkali waste (chiefly calcium sulphide), for the production of a matte of nickel and iron, together with a slag, consisting of silicates of lime, magnesia, and other bases. This matte, which generally contains about 50 per cent. of nickel, 30 per cent. of iron, and 20 per cent. of sulphur, is either blown in small Bessemer converters similar to those used for enriching copper mattes (p. 411), or is smelted in reverberatory furnaces together with a siliceous flux, yielding in both cases a rich pure

[1] Steinhart, *Trans. Inst. Min. and Met.*, 1905–6, **15**, 230.

nickel sulphide, containing 80 per cent. of nickel, and a siliceous iron slag containing a small amount of nickel.

It is, however, impossible to blow this nickel sulphide to the metal, as can be done with copper sulphide, on account of reactions which yield NiO taking place more easily and at a lower temperature than those yielding metallic nickel. The nickel sulphide has therefore to be carefully roasted, generally twice, sometimes with the addition of sodium nitrate, and the nickel oxide washed and dried. The oxide is then pressed into the form of small cubes, and these are strongly ignited with charcoal powder. The reduction takes place from the outside, the metal absorbing carbon and retaining the form of the cubes. The operation is usually carried on in clay crucibles standing on the hearth of a reverberatory furnace, or in a special furnace [1] in which the reduction may be carried on continuously. This consists of a furnace through which vertical fire-clay tubes pass; these tubes are charged at the top with the mixture of crude oxide and coal, and the metal is withdrawn from time to time at the bottom. Commercial nickel contains carbon, as well as small quantities of cobalt, copper, iron, and sulphur.

For sulphides such as the Canadian ores, containing 3 per cent. of nickel and about 2 per cent. of copper, the process is carried out as follows: the ore is first heap-roasted to oxidise the iron and remove the excess of sulphur. The roasted ore is then smelted in a blast furnace, producing a matte containing 36 to 40 per cent. nickel-copper. This matte is then concentrated, either by being again put through the cupola with a siliceous flux, or by being blown in a converter, to an 80 per cent. nickel-copper matte.

The separation of the nickel from the copper is effected by what is known as "tops and bottom" smelting, by means of an alkaline sulphide. The matte is mixed with coke and sodium sulphate (salt-cake), 30 tons of salt-cake and 7 tons of coke being used for 50 tons of matte, and is charged into a magnesia-lined open-hearth reverberatory furnace. The mixture is melted down and allowed to stand for five hours in the furnace, being frequently poled. Practically complete solution of the copper sulphide, and any iron sulphide present, is thus effected in the sodium sulphide formed from the salt-cake. The molten charge is then tapped from the furnace and allowed to separate in moulds, or the two strata are

[1] *Ber. Entw. Chem. Ind.*, **7**, 866.

tapped separately from the furnace. The nickel sulphide thus obtained may be roasted and reduced as already described. A small amount of nickel is also extracted by a wet method as described under cobalt (p. 1276).

An extremely interesting process was introduced by Mond,[1] which depends on the formation of the volatile nickel carbonyl, $Ni(CO)_4$, when the finely divided metal is exposed to the action of carbon monoxide at 80°. The Canadian matte is roasted and, after the extraction of the copper by means of sulphuric acid, is exposed to the reducing action of water gas at a temperature not exceeding 400°. The reduced metal is then passed by air-tight conveyers to the "volatiliser," in which it passes downwards over a series of shelves, where it is exposed at a temperature of 80° to an ascending current of carbon monoxide. This gas is prepared by passing the flue gas from a boiler through potassium carbonate solution, boiling the solution, and leading the pure carbon dioxide given off over incandescent coke. The gas leaving the volatiliser contains nickel carbonyl and is passed through tubes or chambers heated to 180°, in which the nickel is deposited in the pure state, the carbon monoxide being regenerated and passing back to the volatiliser:

$$Ni(CO)_4 = Ni + 4CO.$$

In practice, small quantities of magnesium are often added to molten nickel; this is found to make the metal very fluid before casting, and also renders it malleable, and free from blow-holes due to gas.

Pure nickel can be prepared, according to Winkler,[2] by electrolysing a solution of the pure sulphate containing ammonium sulphate and ammonia, a cathode of highly polished nickel being used, and the current passed until the nickel separates from the electrode in thin plates. It is then heated in a current of pure dry hydrogen.

The production and consumption of metallic nickel is rapidly increasing, as is shown by the following figures, giving the world's production of the metal:

1868	700 tons
1895	4762 „
1900	7526 „
1904	12,000 „
1910	20,000 „

[1] *J. Soc. Chem. Ind.*, 1895, **14**, 945. [2] *Zeit. anorg. Chem.*, 1894, **8**, 1.

596 *Properties.*—Nickel is a lustrous silver-white metal with a steel-grey tinge. It is very hard and takes a high polish, and may easily be rolled out into thin plates and drawn into wire. The pure metal melts at 1452°, but may be welded below its melting point, and distils in the electric furnace more readily than cobalt.[1] As in the case of iron, when the metal contains carbon it is less malleable and more readily fusible. It has a sp. gr. of 8·8 to 8·9, and its average specific heat between 15° and 100° is 0·10842.

Nickel oxidises only with difficulty, even on heating in the air. It decomposes steam very slowly at a red heat with formation of the monoxide, which is also formed when the metal is heated at 200° in nitric oxide.[2] It is slowly soluble in hydrochloric or dilute sulphuric acid, and does not dissolve quickly even in the concentrated acid. On the other hand, it dissolves readily in dilute nitric acid; but if it be dipped into the concentrated acid it becomes "passive" as does iron. Nickel is attracted by the magnet below 360°, and readily assumes a polar condition. It is capable of absorbing about 17 times its volume of hydrogen. Nickel is now largely employed for plating and for the manufacture of alloys, among which nickel steel, nickel-chrome steel, and German silver are the most important. The unalloyed metal, containing 98·7 per cent. of nickel and cobalt, was adopted in 1892 by the Government of Austria-Hungary for the production of minor coins, and has since been largely used for this purpose by other countries. It is employed also for the manufacture of crucibles which can be used in many laboratory operations, instead of those made of the more costly platinum.

Electro-nickel Plating.—Pure nickel is used as the positive pole in processes for the electro-deposition of nickel, which are especially valuable for coating iron and steel with a thin film of pure nickel. If the coating be well deposited the metal scarcely undergoes any oxidation, but it is found to adhere better when a layer of copper is first deposited on the iron. The process of nickel-plating was first applied to fire-arms in order to preserve them from rusting. Now, however, it is also used for covering various parts of machines, locks, keys, surgical instruments, and other fine iron- and steel-work. A great variety of proposals have been made for the preparation of the liquid used in this process, but the only bath which is practically useful is a

[1] Moissan, *Compt. rend.*, 1906, **142**, 425.
[2] Sabatier and Senderens, *Compt. rend.*, 1892, **114**, 1429.

solution of pure nickel ammonium sulphate, saturated at a temperature of 20–25°.[1]

Alloys of Nickel.

597 In 1825 Thénard in his *Traité de Chimie* remarked that nickel was not employed for any practical purpose, although Engeström had pointed out so long ago as 1776 that Chinese packfong is an alloy of copper, zinc, and nickel. Packfong, or rather Pack-Tong, means white copper, and Tong-Pack probably means the same thing, although in Europe this name, changed to tomback, is employed to describe a particular kind of brass. Since the middle of the eighteenth century a white alloy had been prepared at Suhl, in Hanneberg, from old copper slag; and Brandes in 1823 showed that this white copper consisted chiefly of an alloy of copper and nickel, and thus commenced the manufacture of nickel alloys known under the name of German silver, nickel silver, or argentan, a trade which has now attained large dimensions. The nickel industry received a further impulse from the application of copper-nickel alloys to the manufacture of small coin, which was first introduced into Switzerland in 1850. The Swiss pieces of twenty, ten, and five centimes contain respectively fifteen, ten, and five per cent. of silver alloyed with 10 parts of nickel and 12·4 of zinc, the residue being made up of copper. These proportions are, however, not constant, as in the melting more or less zinc volatilises. A yellow alloy containing twelve of nickel to eighty-eight of copper was adopted in 1856 by the United States Government for the one cent pieces, and in 1860 the Belgian Government instituted a nickel-copper coinage, containing twenty-five of the former to seventy-five of the latter metal, this same alloy being adopted in 1866 by the United States for the five and ten cent pieces, by Brazil in 1872, and by the German Government in 1873 for the five- and ten-pfennig pieces.

The advantages of nickel coinage are, in the first place, that the metal is more valuable than copper, and, therefore, for the same value, the coins can be of smaller size; secondly, that the alloy is hard and the coin wears well; thirdly, that the alloy requires experienced workmen to prepare it in the homogeneous condition; and, lastly, that in consequence of its hardness it requires powerful machinery for its manufacture.

It is a very remarkable fact that a coin of the Bactrian King

[1] *Ber. Entw. Chem. Ind.*, i., 874

Euthydemos, who reigned about 235 B.C., analysed by Flight,[1] possesses a very similar composition to the alloy in question, viz.: 77·58 per cent. of copper, and 20·04 per cent. of nickel.

The above alloys of nickel, on fusing, absorb a considerable quantity of gas, and the higher the temperature and the percentage of nickel the greater is the quantity absorbed. Künzel found that if an alloy of eighty parts of copper and twenty of nickel be fused in a crucible half filled with the mixture, and this quickly cooled, the mass froths up from the evolution of gas, and runs over the top of the crucible. If a copper-nickel alloy be granulated in water, yellow globules are obtained, and these are frequently so thin that they float on the surface of the water.[2]

Nickel Silver, or *German Silver*, is an alloy of copper, nickel, and zinc, containing its constituents in varying proportions according to the method of preparation and the articles for which it is used. As a rule five parts of copper, two of nickel, and two of zinc are used, thus giving rise to an alloy which has the appearance of silver alloyed with one-quarter of copper. In Sheffield, eight parts of copper, 3·5 of zinc, and three of nickel are employed. A commoner and yellowish alloy is obtained when less nickel is used, whereas if more nickel be employed the alloy has a bright white colour, and takes a high silvery polish. The addition of 2·5 per cent. of iron makes the alloy whiter, but also harder and more brittle.

The following table gives the composition of several of these alloys: No. I. is Chinese packfong analysed by Fyfe; II. the same, by Kefferstein; III. German silver by Bolley: IV.–VI. various samples of nickel silver used in Birmingham for articles to be plated, and analysed by Louyet; VII. an alloy from Sheffield distinguished by extraordinary elasticity and used for the friskets of printing presses, analysed by Elsner; and VIII. an alloy used for strong castings, such as high pressure steam fittings.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Copper .	40·4	26·3	54·0	63·34	62·40	62·63	57·4	70·0
Zinc . .	25·4	36·8	28·0	17·01	22·15	26·05	25·0	10·0
Nickel .	31·6	36·8	18·0	19·13	15·05	10·85	13·0	20·0
Iron . .	2·6	—	—	trace	trace	trace	3·0	—
	100·0	99·9	100·0	99·48	99·60	99·53	98·4	100·0

[1] The *Numismatic Chronicle*, **8**, 305; and *Pogg. Ann.*, 1870, **139**, 507.

[2] *Ber. Entw. Chem. Ind.*, i., 867.

In preparing nickel silver it is usual to melt the zinc with half the weight of copper which it is ultimately to contain, this alloy being then cast into thin plates. The other half of the copper is then fused with the nickel under a layer of charcoal powder, and the copper-zinc alloy is added. After cooling, the alloy possesses a crystalline structure, and this is got rid of by hammering and rolling, again heating, and allowing to cool. When it has once lost its crystalline structure it can be worked like brass, and although it is harder and tougher it may be rolled out to foil and drawn to wire. Hence this alloy is used for a great number of purposes, as it is much cheaper than silver, and less apt to be discoloured. On the other hand, it is more readily attacked by acid liquids, and for this reason nickel silver articles employed for household use are generally covered with a coating of silver. The addition of small quantities of aluminium has been shown to improve greatly the quality and appearance of nickel silver.

An alloy of nickel with four parts of copper is used for the casing of bullets to be employed with small-bore rifles.

Monel metal is an alloy possessing remarkable mechanical properties and containing about 67 per cent. nickel, 28 per cent. copper, and 5 per cent. iron and manganese.

The addition of nickel to copper greatly increases its electrical resistance, the maximum resistance being obtained with about 40 per cent. of nickel; the resulting alloy is known as Constantan, on account of its low temperature coefficient.

Other high resistance alloys containing nickel are Platinoid, consisting of 60 per cent. copper, 24 per cent. zinc, 14 per cent. nickel, and 1 to 2 per cent. tungsten, and Rheostan, containing 52 per cent. copper, 18 per cent. zinc, 25 per cent. nickel, and 5 per cent. iron.

COMPOUNDS OF NICKEL.

Nickel and Oxygen.

598 A large number of different oxides of nickel have been described, the most important being the monoxide, NiO, which is the only one yielding a corresponding series of salts. In addition, the sesquioxide, Ni_2O_3, has been prepared, and peroxides are obtained by the electrolytic oxidation of the metal. Tri-

nickel tetroxide,[1] Ni_3O_4, has been described together with several other oxides such as Ni_4O_7,[2] Ni_5O_7,[3] and Ni_3O_5,[4] as well as the suboxides, Ni_2O [5] and Ni_3O,[6] but these are probably mixtures of the monoxide with peroxide in the one case and nickel in the other.

Nickel Monoxide or Nickelous Oxide, NiO.—This substance occurs as bunsenite at Johanngeorgenstadt in Saxony, in vitreous translucent pistachio-green regular octahedra having a specific gravity of 6·398. It may be obtained by strongly heating the hydroxide, sesquioxide, carbonate, or nitrate, in the form of a green crystalline powder, which becomes deep-yellow on heating. If nickel borate be ignited with lime in a pottery furnace and the mass treated with hydrochloric acid, nickel oxide remains behind in green cube-octahedra which have a specific gravity of 6·8 (Ebelmen), whilst if the metal be ignited in a current of steam, pale olive-green crystals of the oxide are formed. When heated in the air nickelous oxide at first absorbs oxygen, but loses it again at a higher temperature, whilst in the electric furnace it melts and solidifies in green crystals.[7] It is readily reduced by hydrogen at 220°,[8] by carbon monoxide at 120°, and by solid carbon at 450°. The dissociation pressures of nickelous oxide have been measured between 800° and 1245°.[9]

Nickel Hydroxide, $Ni(OH)_2$, is thrown down when a solution of a nickel salt is heated with potash or soda, as an apple-green precipitate slightly soluble in water. It dissolves in ammonia with a blue colour, and separates out as a green crystalline powder on boiling the ammoniacal solution.

The salts of nickel are derived from the monoxide. In the anhydrous condition, and formed from colourless acids, they are usually yellow-coloured, whilst in the hydrated state they possess an apple-green to an emerald-green colour. The soluble normal salts have a slightly acid reaction and a sweetish astringent metallic taste, and act as emetics.

[1] Baubigny, *Compt. rend.*, 1878, **87**, 1082; Dudley, *J. Amer. Chem. Soc.*, 1896, **18**, 901; Bellucci and Rubegni, *Atti R. Accad. Lincei*, [5], 1906, **15**, ii., 778. [2] Wicke, *Jahresb.*, 1865, 267.

[3] Schröder, *Journ. Chem. Soc.*, 1890, **58**, 1213.

[4] *Chem. News*, 1879, **39**, 81. [5] Müller, *Pogg. Ann.*, 1869, **136**, 59.

[6] Moore, *Chem. News*, 1895, **71**, 81.

[7] Moissan, *Ann. Chim. Phys.*, 1880, [5], **21**, 199; *Compt. rend.*, 1892, **115**, 1034.

[8] Ipatieff, *J. pr. Chem.*, 1908, **77**, 513.

[9] Foote and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1344.

Nickel Sesquioxide, Ni_2O_3, is a black powder obtained by gentle ignition of the nitrate or carbonate in the air, and is converted at a higher temperature into the monoxide. When the sesquioxide is heated in the oxy-coal-gas flame it yields metallic nickel,[1] which on cooling becomes covered with a film of oxide. It dissolves in sulphuric and nitric acids with evolution of oxygen, and in hydrochloric acid with evolution of chlorine, whilst nitrogen is evolved when it is acted upon by ammonia:

$$3Ni_2O_3 + 2NH_3 + 3H_2O = 6Ni(OH)_2 + N_2.$$

When potassium is burnt in the air in nickel vessels, and the product treated with water, black prisms remain having the composition $Ni_2O_3,2H_2O$, which rapidly oxidise organic substances.[2] It appears most probable that the sesquioxide is a compound of the monoxide and dioxide, NiO,NiO_2, and is to be regarded as nickelous nickelite.

When chlorine is passed through nickelous hydroxide suspended in water, or when a solution of a nickel salt is warmed with an alkali hypochlorite, a black precipitate is formed which is generally regarded as *nickel trihydroxide*, $Ni(OH)_3$, corresponding to the sesquioxide. According to Bellucci and Clavari,[3] however, this substance is in reality the hydrated dioxide, NiO_2,xH_2O, which rapidly loses oxygen.

Nickel Dioxide, NiO_2, has not been prepared in the anhydrous state, but a compound of this oxide and baryta termed *barium nickelite*, $BaO,2NiO_2$, is formed when barium carbonate is strongly heated with nickel sesquioxide in the electric furnace. It forms dark coloured crystals of sp. gr. 4·8, which are rapidly decomposed by hot water and dissolve in hydrochloric acid with evolution of chlorine.[4]

A peroxide of nickel, of uncertain composition, is formed by the electrolytic oxidation of the metal, and plays a part in the Jungner-Edison accumulator.[5] According to Hollard[6] the

[1] Read, *Journ. Chem. Soc.*, 1894, **65**, 314.

[2] Hofmann and Hiendlmaier, *Ber.*, 1906, **39**, 3184.

[3] *Gazz.*, 1905, **14**, ii., 234; *Atti R. Accad. Lincei*, 1907, [5], **16**, i., 647; compare Pellini and Meneghini, *Zeit. anorg. Chem.*, 1908, **60**, 178; Tanatar, *Ber.*, 1909, **42**, 1516; Tubandt and Riedel, *ibid.*, 1911, **44**, 2565; *Zeit. anorg. Chem.*, 1911, **72**, 219.

[4] Dufau, *Compt. rend.*, 1896, **123**, 495.

[5] See Zedner, *Zeit. Elektrochem.*, 1905, **11**, 809; 1906, **12**, 463; 1907, **13**, 752; Foerster, *ibid.*, 1907, **13**, 414; 1908, **14**, 17; Riesenfeld, *ibid.*, 1906, **12**, 621.

[6] *Compt. rend.*, 1903, **136**, 229.

tetroxide, NiO_4, is produced by the electrolysis at 70° of a very dilute solution of a nickel salt containing chromic acid and an alkali pyrophosphate.

Nickel and the Halogens.

599 *Nickel Fluoride*, NiF_2, is obtained by dissolving the hydroxide or carbonate in hydrofluoric acid and evaporating, when blue-green crystals of $NiF_2,3H_2O$ separate.[1] These are decomposed by boiling water with formation of an insoluble pale-green oxyfluoride.

The anhydrous fluoride is obtained by heating the chloride with ammonium fluoride in a current of hydrogen fluoride.[2] It forms volatile green prisms of specific gravity 4·63, which are not attacked by mineral acids, but are reduced by hydrogen.

Nickel fluoride forms double salts with the alkali fluorides.

Nickel Chloride, $NiCl_2$.—Finely divided nickel burns with a bright light when it is slightly heated in dry chlorine gas, forming yellow scales resembling mosaic gold. If a solution of the oxide or carbonate in hydrochloric acid be evaporated to dryness, the anhydrous chloride is obtained as a yellow earthy mass which dissolves readily in water with evolution of heat. On gently heating for some time in the air it evolves chlorine, leaving a residue of the oxide. In absence of air, on the other hand, it can be sublimed, and is then obtained in golden scales which, when boiled for some time with caustic potash, are completely converted into the hydroxide. They become gradually coloured green on exposure to the air owing to the absorption of moisture, and are then easily soluble in water. The salt, $NiCl_2,6H_2O$, is obtained in short six-sided prisms on concentrating the solution; these are easily soluble in water and in alcohol. The hexahydrate is stable in contact with its saturated solution up to about 70°.[3]

The anhydrous chloride absorbs ammonia at the ordinary temperature, swelling up to a white powder, possessing a slightly violet tinge, and having the composition $NiCl_2,6NH_3$. The same compound is obtained in blue octahedra by dissolving the chloride in ammonia and allowing the solution to cool. This salt readily evolves ammonia when exposed to the air. It is

[1] Compare Costachescu, *Ann. Sci. Univ. Jassy*, 1911, **7**, 5.
[2] Poulenc, *Compt. rend.*, 1892, **114**, 1426.
[3] Étard, *Ann. Chim. Phys.*, 1894, [7], **2**, 539.

easily soluble in water, but less so in strong alcohol. Similar compounds are formed by the bromide and iodide.

Nickel Bromide, $NiBr_2$.—Finely divided nickel absorbs bromine vapour when heated in it, becoming incandescent. In absence of air, the bromide sublimes in golden scales which deliquesce on exposure. The solution, which is also obtained by bringing the metal in contact with bromine and water, gives on evaporation deliquescent needles of $NiBr_2,3H_2O$.

Nickel Iodide, NiI_2.—If nickel powder reduced in hydrogen be heated with iodine, or if the hydroxide be dissolved in hydriodic acid, the solution evaporated to dryness in absence of air, and the solid heated, nickel iodide sublimes in iron-black scales. The solution when evaporated to a syrup deposits bluish-green, very deliquescent prisms having the composition $NiI_2,6H_2O$.

Nickel Chlorate, $Ni(ClO_3)_2$, forms three hydrates containing respectively, 6, 4, and 2 molecules of water.[1] The *perchlorate* also has been described.

Nickel Iodate, $Ni(IO_3)_2$, forms a tetrahydrate and two dihydrates. The tetrahydrate loses water, iodine, and oxygen below 100°.[2]

Nickel and Sulphur.

600 *Nickel Monosulphide*, NiS, occurs as millerite, being occasionally found in brass-yellow rhombohedra, but more commonly in capillary crystals. When nickel and sulphur are heated together above the melting point of the latter, this same compound is formed with incandescence as a bronze-yellow brittle mass which is not soluble in hydrochloric or sulphuric acid, but dissolves in nitric acid and aqua regia. The black hydrated sulphide is precipitated when ammonium sulphide is added to a nickel salt. This is difficultly soluble in hydrochloric acid, but slightly soluble with a brownish colour in ammonia, as well as in yellow ammonium sulphide and other alkaline polysulphides; it is precipitated from these solutions on exposure to the air, or on addition of acetic acid. In the moist state it oxidises readily on exposure to the air. When a solution of a nickel salt is heated with sodium thiosulphate, the monosulphide is obtained in the form of a dense black precipitate which does not undergo alteration on exposure

[1] Meusser, *Ber.*, 1902, **35**, 1414. [2] Meusser, *Ber.*, 1901, **34**, 2432.

to the air, and which is not acted upon by boiling hydrochloric acid.

The sulphide is not precipitated by sulphuretted hydrogen in presence of dilute hydrochloric acid, and yet the precipitated sulphide, when obtained from an alkaline solution, is found to be insoluble in dilute hydrochloric acid. It appears probable, therefore, that a rapid change occurs in the freshly precipitated sulphide, and that it thus passes into a form which is insoluble in dilute hydrochloric acid.[1]

The freezing point curve for mixtures of nickel and sulphur[2] shows that the only compound capable of existence in contact with the melt is Ni_3S_2, melting at 787°. The compounds NiS, Ni_3S_4, and NiS_2 also exist, but dissociate below the melting point.

Nickel Subsulphide, Ni_2S, is obtained as a bronze-yellow, non-crystalline mass when the monosulphide is heated in the electric furnace, and on further heating loses the remainder of the sulphur forming metallic nickel.[3]

Linnaeite, $(Ni,Co,Fe)_3S_4$, is an important nickel ore occurring at various places in considerable masses (see p. 1284).

Nickel Sesquisulphide, Ni_2S_3.—A black precipitate having approximately this composition is obtained by acting on nickel carbonyl with sulphur dissolved in carbon disulphide.[4]

Nickel Disulphide, NiS_2, is obtained as an impalpable iron-grey powder by strongly heating a mixture of nickel carbonate, potassium carbonate, and sulphur, the residue being lixiviated with water.

Nickel Sulphate, $NiSO_4$.—This salt was first obtained in the pure and crystalline condition in 1775 by Bergman. In order to prepare it, nickel or its hydroxide or carbonate is dissolved in dilute sulphuric acid. The evaporation of the neutral solution at the ordinary temperature yields green rhombic prisms of the heptahydrate, $NiSO_4,7H_2O$, isomorphous with magnesium sulphate. The heptahydrate is known also as nickel vitriol, or morenosite, occurring in acicular crystals, and as a fibrous efflorescence on certain nickel ores. On prolonged exposure to the air the heptahydrate changes into aggregates of blue tetragonal crystals of the hexahydrate. This latter com-

[1] See Thiel and Ohl, *Zeit. anorg. Chem.*, 1909, **61**, 396.
[2] Bornemann, *Metallurgie*, 1908, **5**, 13; 1910, **7**, 667.
[3] Mourlot, *Compt. rend.*, 1897, **124**, 768.
[4] Dewar and Jones, *Journ. Chem. Soc.*, 1904, **85**, 211.

pound may be prepared by the slow evaporation at the ordinary temperature of solutions containing 30 per cent. sulphuric acid; it is stable in contact with its saturated solutions between 32° and 53°.[1] If the heptahydrate or the blue hexahydrate is left in contact with the saturated solution above 54°, it is converted into bright-green monoclinic crystals, which have also the composition $NiSO_4,6H_2O$. At a temperature about 118° the hexahydrate is transformed into the dihydrate, and if heated above 280°, the salt loses the whole of its water. One hundred parts of saturated solution contain (Steele and Johnson):

At	0°	15°	30°	44·7°	50°	60°	80°	99°	
$NiSO_4$	21·4	25·5	29·8	32·4	33·4	35·4	38·7	43·4	parts.

Various basic sulphates have been described.[2]

The anhydrous sulphate absorbs ammonia, becoming strongly heated and increasing in bulk, forming a violet-white powder with the composition $NiSO_4,6NH_3$. On dissolving the sulphate in strong ammonia and cooling, or allowing the solution to evaporate over sulphuric acid, transparent dark-blue tetragonal prisms crystallise out having the composition $NiSO_4,4NH_3,2H_2O$. A compound of the formula $2NiSO_4,10NH_3,7H_2O$ has also been described.

Nickel Ammonium Sulphate, $(NH_4)_2SO_4,NiSO_4,6H_2O$.—This salt is employed in the process of nickel-plating. It is obtained by dissolving nickel, free from iron and copper, in dilute sulphuric acid, and adding ammonium sulphate to the concentrated acid solution. The crystalline paste which is deposited is washed with cold water and purified by recrystallisation. It crystallises in short monoclinic prisms. One hundred parts of water dissolve (Link):

At	3·5°	16°	20°	30°	40°	50°	68°	85°	
$(NH_4)_2SO_4,NiSO_4$	1·8	5·8	5·9	8·3	11·5	14·4	18·8	28·6	parts.

The salt is almost insoluble in an acidified solution of ammonium sulphate (Thomson). Many other double salts are known.

[1] Steele and Johnson, *Journ. Chem. Soc.*, 1904, **85**, 113.
[2] Pickering, *Journ. Chem. Soc.*, 1907, **91**, 1985.

Nickel and the Elements of the Nitrogen Group, and Boron.

601 *Nickel Nitride* is obtained by the action of excess of ammonia on metallic nickel at 400–600°, and forms a black powder, which readily dissolves in dilute sulphuric and hydrochloric acids.[1] The composition of the product is intermediate between those corresponding to the formulæ Ni_3N and Ni_5N_2.

Nitronickel, $Ni_2(NO_2)$, is formed as a black mass mixed with oxide when nitrogen peroxide is passed over reduced nickel, and in its properties resembles the corresponding cobalt compound (p. 1286).[2]

Nickel Nitrite, $Ni(NO_2)_2$, is obtained in solution by the decomposition of the sulphate with barium nitrite. It is a very unstable compound, but forms with potassium nitrite the easily soluble double salt, $4KNO_2,Ni(NO_2)_2$. This is obtained in brownish-red octahedra by mixing a concentrated solution of the nitrite with an excess of potassium nitrite. When potassium nitrite is added to a nickel solution containing a calcium salt, a yellow crystalline precipitate of $2KNO_2,Ca(NO_2)_2,Ni(NO_2)_2$ is formed, which possesses great similarity to potassium cobaltinitrite (see p. 1286), and if a solution contain a sufficient quantity of calcium together with nickel and cobalt, the whole of the nickel, as well as the cobalt, may be thrown down by potassium nitrite. This fact must be remembered in the separation of the two metals.

Nickel Nitrate, $Ni(NO_3)_2,6H_2O$, crystallises in green monoclinic tablets which dissolve in two parts of cold water and in alcohol, and effloresce on exposure to dry air, deliquescing however, in moist air. Hydrates with $3H_2O$ and $9H_2O$ have also been obtained.[3] Anhydrous nickel nitrate is a pale greenish-yellow powder, which begins to evolve nitrous fumes at 105–110°.[4]

Nickel Phosphides.—When nickel and phosphorus are heated in the electric furnace the compound Ni_2P is obtained in transparent grey needles of sp. gr. 6·3,[5] insoluble in all acids except a mixture of nitric and hydrofluoric acids. A phosphide

[1] Beilby and Henderson, *Journ. Chem. Soc.*, 1901, **79**, 1251.
[2] Sabatier and Senderens, *Bull. Soc. chim.*, 1893, [3], **9**, 669.
[3] Funk, *Zeit. anorg. Chem.*, 1899, **20**, 409.
[4] Guntz and Martin, *Bull. Soc. chim.*, 1909, **5**, 1004.
[5] Maronneau. *Compt. rend.*, 1900, **130**, 656.

of the same composition is prepared in the wet way as a black precipitate by adding nickel chloride to a boiling solution of potash containing some phosphorus and tartaric acid. Compounds of the formulæ P_2Ni_5, P_2Ni_3, P_3Ni_2, PNi_3, P_2Ni, P_3Ni, have also been described.[1]

Nickel Arsenides.—These two elements fuse together readily to form brittle alloys, some of which occur as minerals. Of these the most important is kupfer-nickel, niccolite, or nickeline, NiAs, which is found massive, and also, although less frequently, crystallised in hexagonal pyramids. It has a light copper-red colour, and is an important ore of nickel, being found in various localities in Europe and America. Chloanthite, $(Ni,Co,Fe)As_2$, is another nickel arsenide occurring together with the preceding. The study of the freezing point curve for mixtures of nickel and arsenic indicates the existence of the compounds NiAs, Ni_3As_2, and Ni_5As_2.[2]

The Phosphates of Nickel are insoluble in water, and more or less soluble in the mineral acids. The *arsenates* possess similar properties, and some of them occur in the mineral kingdom.

Nickel Boride, NiB, is prepared in the electric furnace from its constituents, and forms brilliant prisms of specific gravity 7·39. It is decomposed by fused alkalis and by water vapour at a dull red heat.[3] The compounds Ni_2B and NiB_2 have also been described.[4]

Nickel and the Elements of the Carbon Group.

602 *Nickel Tetracarbonyl*, $Ni(CO)_4$.—When carbon monoxide is passed over metallic nickel at about 350–400°, carbon dioxide is formed and carbon liberated, but at a lower temperature the metal unites with carbon monoxide to form nickel tetracarbonyl. This substance is best prepared by reducing nickel oxide in hydrogen at about 400° in a combustion tube, allowing it to cool to 30–80°, and then passing carbon monoxide over the reduced metal. When the issuing gas is cooled with

[1] See Granger, *Compt. rend.*, 1896, **122**, 1484; 1896, **123**, 176; Konstantinoff, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 742; Jolibois, *Compt. rend.*, 1910, **150**, 106.

[2] Friedrich and Bennigson, *Metallurgie*, 1907, **4**, 200. Compare Vigouroux, *Compt. rend.*, 1908, **147**, 426.

[3] Moissan, *Compt. rend.*, 1896, **122**, 424.

[4] Binet du Jassonneix, *Compt. rend.*, 1907, **145**, 240.

salt and ice it deposits the nickel carbonyl, the excess of the gas being repeatedly passed over the nickel until no more of the compound is formed. The metal is then again heated in hydrogen at 400°, cooled, and treated with carbon monoxide, the whole process being repeated as often as desired; about 10–15 grams are obtained at each operation.[1] If carbon monoxide under high pressure is employed, the nickel may be heated much more strongly.[2] Thus under 100 atmospheres the nickel carbonyl produced is not decomposed even at 250°.

Nickel tetracarbonyl is a colourless liquid, having a specific gravity of 1·3185 at 17°; it boils at 43·2° under 760 mm. pressure, and solidifies at −25°, forming needle-shaped crystals. It has the normal vapour density of 6·01 at 50°, but explodes at 60°, some carbon dioxide being formed and carbon liberated. When diluted with an inert gas the vapour does not explode, and undergoes decomposition less readily;[3] with carbon monoxide as diluent it has nearly the normal vapour density at 100°, and dissociation is not complete at 182°. When gas containing the vapour is passed through a heated tube, pure metallic nickel is deposited with liberation of carbon monoxide.

It is soluble in alcohol, benzene, chloroform, and carbon tetrachloride, and is not acted on by dilute aqueous acids or alkalis. It is not decomposed by water free from air, but dissolves to the extent of 18 mgm. per 100 grams of water at 9·8°; dissociation into nickel and carbon monoxide takes place slowly when the solution is preserved. In the presence of air it undergoes oxidation, nickel hydroxide being formed together with a white compound of unknown constitution containing carbon,[4] which may possibly be a basic carbonate.[5] It is rapidly decomposed by the halogens, yielding carbon monoxide and the nickel halide; concentrated sulphuric acid converts it into nickel sulphate with evolution of hydrogen and carbon monoxide, and it is rapidly oxidised by dry concentrated nitric acid. Dry hydrogen chloride and bromide attack it only very slowly, but dry hydrogen iodide yields nickel iodide, hydrogen, and carbon monoxide. With sulphur dissolved in carbon disulphide a sulphide having approximately the composition Ni_2S_3 is formed, whilst sulphuretted

[1] Mond, Langer, and Quincke, *Journ. Chem. Soc.*, 1890, **57**, 749.
[2] Dewar, *Journ. Chem. Soc.*, 1904, **86**, ii, 488.
[3] Dewar and Jones, *Proc. Roy. Soc.*, 1903, **71**, 427.
[4] Berthelot, *Compt. rend.*, 1891, **112**, 1343; **113**, 679.
[5] Armit, *Journ. Hygiene*, 1907, **7**, 525.

hydrogen yields nickel monosulphide.[1] When nickel carbonyl and thiocarbonyl chloride are allowed to react, carbon monosulphide, or a polymeride of this substance, is produced.[2] As already mentioned (p. 1300), the formation and subsequent decomposition of nickel carbonyl is made use of on the large scale in the Mond process for extracting nickel from its ores.

The vapour of nickel tetracarbonyl has a very poisonous action. When inhaled in small quantities it produces toxic symptoms of a very definite type. The lethal dose for men is unknown, but for animals (rabbits, dogs, cats, etc.) it varies between 0·018 and 0·04 volume per cent. of the vapour in air, inhaled for 65 to 90 minutes. The substance is decomposed in the lungs into carbon monoxide and a nickel compound, which is possibly the hydrated basic carbonate. The carbon monoxide available is not sufficient to produce any symptoms, and the toxic effect is entirely due to the nickel content.[3]

Nickel Carbonate, $NiCO_3$, is obtained in the form of pale-green, microscopic rhombohedra, by heating nickel chloride solution with calcium carbonate to 150°. When a nickel nitrate solution is mixed with a solution of sodium bicarbonate saturated with carbon dioxide, and this is allowed to stand at a low winter temperature, microscopic monoclinic crystals of $NiCO_3,6H_2O$ are formed, which lose their water readily on warming. When a nickel solution is precipitated with an alkali carbonate, basic salts of varying composition are thrown down in the form of pale-green precipitates.

Nickel Cyanide, $Ni(CN)_2$, is an apple-green precipitate easily soluble in an excess of potassium cyanide with formation of the crystalline double salt, $Ni(CN)_2,2KCN$. This is again decomposed by dilute acids with separation of nickel cyanide. No stable salts corresponding to the ferro- and ferri-cyanides are formed.

Nickel Silicide, Ni_2Si, is obtained by heating an excess of nickel with silicon in the electric furnace until the greater part of the metal has been volatilised, and then treating the residue with dilute nitric acid. It is a steel-grey, crystalline powder with a metallic appearance, and has the specific gravity 7·2. It is readily attacked by fluorine, and dissolves in hydro-

[1] Dewar and Jones, *Journ. Chem. Soc.*, 1904, **85**, 203.
[2] Dewar and Jones, *Proc. Roy. Soc.*, A, 1910, **83**, 408.
[3] Armit, *Journ. Hygiene*, 1907, **7**, 525; 1908, **8**, 565.

fluoric acid and in aqua regia.[1] The method of thermal analysis, controlled by microscopic observations, indicates the existence of the following compounds of nickel and silicon: Ni_3Si, Ni_2Si, Ni_3Si_2, NiSi, and Ni_2Si_3.[2]

The Nickel Silicates occur in nature. Rewdanskite occurs at Rewdansk in the Urals, and is worked for nickel. It is an earthy mineral which consists chiefly of $(Ni,Fe,Mg)_3Si_2O_7,2H_2O$, and contains about 18 per cent. of nickel. Garnierite, $2(Ni,Mg)_5Si_4O_{13},3H_2O$, occurs in New Caledonia, and is now largely worked up for nickel in France. It contains 24 per cent. of nickel (Liversidge).

The *orthosilicate*, Ni_2SiO_4, is formed in greenish-yellow crystals when the oxide and chloride are heated with amorphous silica.[3]

Detection and Estimation of Nickel.

603 Nickel compounds behave in a similar manner to those of iron and cobalt when heated with reducing agents before the blowpipe. An infusible magnetic powder is produced, and when this is dissolved in a drop or two of dilute nitric acid and evaporated to complete dryness, a characteristic green stain is obtained which becomes yellow on further heating. Nickel compounds, moreover, colour the borax bead a brownish-yellow in the oxidising flame, the bead becoming grey and opaque in the reducing flame owing to the separation of metallic nickel.

Nickel is very readily detected with the aid of certain organic reagents. Thus when *a*-dimethylglyoxime, $[(CH_3)C{:}N.OH]_2$, is added to a solution of a nickel salt containing excess of ammonia or of sodium acetate, a scarlet precipitate separates, one part of nickel in 400,000 parts of water being capable of detection in this manner.[4] Cobalt does not give a precipitate with this reagent, nor does it interfere with the reaction unless present in very large excess. This reaction may also be employed for the quantitative estimation of nickel,[5] and, indeed, permits the complete separation of this metal from all other metals belonging to the same analytical group. When dicyano-

[1] Vigouroux, *Compt. rend.*, 1895, **121**, 686; 1906, **142**, 1270.

[2] Guertler and Tammann, *Zeit. anorg. Chem.*, 1906, **49**, 93.

[3] Bourgeois, *Compt. rend.*, 1889, **108**, 1177.

[4] Tschugaeff, *Ber.*, 1905, **38**, 2520, *Compt. rend.*, 1907, **145**, 679; Brunck, *Zeit. angew. Chem.*, 1907, **20**, 834, 1835.

[5] *Loc. cit.*; see also Armit and Harden, *Proc. Roy Soc.*, 1906, B, **77**, 420.

diamide, $C_2N_4H_4$, and then caustic potash are added to a solution of a nickel salt previously acidified with hydrochloric acid, a dense yellow precipitate is produced of nickel dicyanodiamidine, $Ni(C_2N_4H_5O)_2,2H_2O$, which becomes flesh-coloured when heated. In dilute solutions the precipitate forms only on boiling or standing.[1]

The nickel compounds in general give no flame spectrum, but the acetate when moistened with hydrochloric acid gives first a transient purple, followed by a more permanent deep-red colour, the production of the colour taking place in the inner cone of the flame.[2] The chloride yields a characteristic spark spectrum, and the spectrum of the metal also contains many lines, of which a few of the brightest are 5893 in the orange, and 4874, 4866, and 4856 in the green-blue.

Nickel is precipitated in alkaline solution by ammonium sulphide along with the other metals of the iron group, from all of which except cobalt it can be separated by treating the precipitate with dilute hydrochloric acid, in which the sulphides of these two metals are almost insoluble. A characteristic property of nickel sulphide is that it dissolves slightly in yellow ammonium sulphide, forming a dark-coloured solution.

The best method for the qualitative detection of nickel and cobalt is based on Liebig's method for their estimation (see below). For this purpose the sulphides are dissolved in concentrated hydrochloric acid with the addition of a crystal of potassium chlorate, and the solution evaporated nearly to dryness and afterwards diluted with water. Potassium cyanide is then added until the precipitated cyanides re-dissolve, a drop of acetic acid is added and the liquid boiled for a few minutes. The solution then contains potassium cobalticyanide and potassium nickel cyanide. The latter is at once decomposed by sodium hypochlorite in alkaline solution, whereas the former is not attacked by this reagent. The solution is therefore made alkaline with caustic soda and boiled with sodium hypochlorite, when the nickel is precipitated as the black trihydroxide, which may be filtered off, washed, and tested by the borax bead, whilst the cobalt can be detected in the filtrate by evaporating, and testing the residue by one of the dry reactions.

[1] Grossmann and Schück, *Ber.*, 1906, **39**, 3356; *Chem. Zeit.*, 1907, **31**, 335, 911.

[2] Hartog, *British Assoc. Reports*, 1901, 613.

Cobalt is much more readily precipitated in the form of sesquioxide than nickel, a fact which is made use of in the commercial separation of the two. This reaction can also be used for the qualitative and quantitative separation of nickel and cobalt. When bromine water is added to a cold neutral solution of the two metals, the cobalt is rapidly precipitated as the sesquioxide, whilst the nickel remains in solution.[1]

Numerous methods, both gravimetric and volumetric, have been proposed for the quantitative separation and estimation of nickel and cobalt. In addition to the dimethylglyoxime and dicyanodiamide processes, already referred to, the three following gravimetric methods may be described.[2]

Liebig's hydrocyanic acid method[3] may be applied to the quantitative separation of the metals substantially in the form which has been described above. The solution containing potassium cobalticyanide and potassium nickel cyanide may be treated with caustic soda and sodium hypochlorite as there described, or may be boiled with precipitated mercuric oxide, the whole of the nickel being precipitated as a mixture of oxides, which after ignition may be weighed as nickel monoxide. The filtrate is acidified with nitric acid, and mercurous nitrate added in excess. Mercurous cobalticyanide is precipitated and is converted by ignition into tricobalt tetroxide. Both in this and the succeeding methods one of the metals is frequently estimated indirectly. The two are precipitated together by caustic soda from a known volume of solution, and the mixed oxides weighed, the amount of one of the metals being then found by difference.

Another separation of nickel from cobalt depends upon the precipitation of potassium cobaltinitrite (see p. 1286). This is dried at 100° and weighed, and the nickel in the filtrate is precipitated by caustic potash, the precipitate boiled, well washed, and converted by ignition into the monoxide.

A very accurate method depends on the fact that nitroso-β-naphthol, $C_{10}H_6(OH)NO$, yields an insoluble compound with cobalt salts, but not with those of nickel.[4] The solution is therefore acidified with hydrochloric acid, and a solution of this

[1] Taylor, *Mem. Manch. Phil. Soc.*, 1902, **46**, No. 11.

[2] Compare *Zeit. anal. Chem.*, 1891, **30**, 227.

[3] *Annalen*, 1853, **87**, 128.

[4] Ilinski and Knorre, *Ber.*, 1885, **18**, 699; Chapin, *J. Amer. Chem. Soc.*, 1907, **29**, 1029.

reagent in acetic acid added. A very voluminous precipitate is formed, which is well washed and then ignited with a little oxalic acid, the cobalt being finally heated in hydrogen and weighed.

The Atomic Weight of nickel has been frequently determined. Of the older determinations, the most important are those of Russell,[1] Schneider,[2] Dumas,[3] Zimmermann,[4] and Winkler.[5] More recent and accurate determinations were made by Richards and Cushman,[6] who deduced the value 58·69 from the amount of silver required to precipitate the bromine in pure nickel bromide, and the value 58·71 from the weight of nickel produced by the reduction of the same compound in hydrogen. The value now adopted (1913) is 58·68.

The statement made by Krüss and Schmidt[7] that ordinary pure nickel contains another element of higher atomic weight has not been confirmed.

SUB-GROUP (*b*). THE RUTHENIUM GROUP.

Ruthenium. Rhodium. Palladium.

604 The three metals of this group all have a silvery lustre, and combine with oxygen at high temperatures rather more readily than the members of the platinum group; they also melt at a lower temperature. The salts of ruthenium and rhodium correspond to the sesquioxide, M_2O_3, whilst palladium forms two series of salts corresponding to the monoxide and dioxide, the former being the more stable. In addition, ruthenium yields salts of the acidic oxides RuO_3 and Ru_2O_7, and also, unlike the other two, forms a tetroxide, RuO_4.

All three metals give rise to series of ammoniacal bases, the properties and composition of which differ, however, in each case. The ruthenium bases all contain the nitroso-group, NO,

[1] *Journ. Chem. Soc.*, 1863, **16**, 58; *ibid.*, 1869, **22**, 294.
[2] *Pogg. Ann.*, 1857, **101**, 387.
[3] *Ann. Chim. Phys.*, 1859, [3], **55**, 129. [4] *Annalen*, 1885, **232**, 324.
[5] *Zeit. anal. Chem.*, 1867, **6**, 22; *Zeit. anorg. Chem.*, 1893, **4**, 10, 462; 1895, **8**, 1, 291.
[6] *Zeit. anorg. Chem.*, 1898, **16**, 167; 1899, **20**, 352.
[7] *Zeit. anorg. Chem.*, 1892, **2**, 235.

in addition to ammonia; those of rhodium closely resemble the cobalt derivatives, and those of palladium correspond to two of the series yielded by platinum.

RUTHENIUM. Ru = 101·7.

605 In 1828 Osann[1] stated that he had discovered three new metals in the platinum ores from the Ural. To one of these he gave the name of *ruthenium*, from the name of Russia, the country in which it was found. In the following year, however, he withdrew the statement of the existence of one of the metals, and the existence of the other two remained doubtful until Claus, in 1845, examined the question. This chemist proved the existence of a new metal in the platinum ore, and retained for it the name of ruthenium because it was found to be contained in small quantity in the substance termed ruthenium oxide by Osann, which for the most part consisted of silica, zirconia, and the oxides of titanium and iron. Claus investigated the reactions of the metal and a large number of its derivatives.[2]

Ruthenium is found both in platinum ore and in osmiridium, whilst it occurs as sulphide in laurite, Ru_2S_3.[3]

Of the various methods of preparing the metal, that of Deville and Debray[4] is the most interesting, as these chemists obtained it on a large scale, and specially studied its physical properties. For this purpose, the alloy of osmiridium (p. 1361) containing ruthenium is fused with zinc, the regulus then treated with hydrochloric acid, and one part of the finely-divided residue mixed with three parts of barium peroxide and one part of barium nitrate, the mixture being heated for two hours to a temperature somewhat below the melting point of silver. The cold mass is then reduced to an impalpable powder and thrown into dilute hydrochloric acid contained in a stoppered bottle. In this operation the liquid must be kept well cooled in order to prevent the escape of the poisonous vapours of osmium tetroxide, and the operation must be carried on in a

[1] *Pogg. Ann.*, 1828, **14**, 329; 1845, **64**, 197.

[2] *Annalen*, 1845, **56**, 257; 1846, **59**, 234; *Pogg. Ann.*, 1845, **64**, 622; **65**, 200; *Jahresb.*, 1859, 257; 1860, 205; 1861, 320; 1863, 397.

[3] Wöhler, *Annalen*, 1864, **129**, 116.

[4] Deville and Debray, *Compt. rend.*, 1876, **83**, 926; 1879, **89**, 587.

good draught. As soon as the action is over, one part of nitric acid and two parts of sulphuric acid are added to the liquid, the mixture well shaken, the barium sulphate allowed to deposit, and the clear liquid poured off. The residue is washed by decantation, and the liquid distilled until three-fourths of it have passed over. The distillate is worked up for osmium, whilst the concentrated residue, mixed with from two to three parts of ammonium chloride and a small quantity of nitric acid, is dried on the water bath. The residue is then washed with water which is half saturated with ammonium chloride, until the filtrate is colourless. By this treatment ammonium iridichloride, containing some ruthenium, remains behind. This is ignited, and the remaining spongy metallic mass fused for two hours in a silver basin with two parts of nitre and one part of caustic potash. The fused mass is then dissolved in water, and the characteristic orange-red solution of potassium ruthenate treated with nitric acid until the yellow colour has disappeared, when ruthenium oxide separates out; this, however, still contains silicic acid, with some iridium and osmium, and is then ignited in a graphite crucible and fused in the oxy-hydrogen furnace.

Another plan for preparing chemically pure ruthenium depends upon the fact that whilst osmium tetroxide is volatilised in a stream of air, the corresponding volatile tetroxide of ruthenium is only formed by the action of chlorine in alkaline ruthenium solution. Hence the metal, as obtained by other processes, must be heated in a current of oxygen until the whole of the osmium tetroxide has been volatilised and then fused a second time with potash and saltpetre, the mass dissolved in water, saturated with chlorine, and distilled in a stream of chlorine on the water bath, when pure ruthenium tetroxide volatilises. This is then dissolved in caustic potash or in water, reduced by alcohol, and the black precipitate converted into metal by ignition in a stream of pure hydrogen.[1]

In order to obtain the metal in the crystalline state it may be fused in a carbon crucible with from five to six times its weight of tin, the alloy being treated with boiling hydrochloric acid which leaves the compound $RuSn_3$ undissolved; this when ignited in a carbon boat in a current of hydrogen chloride leaves a residue of crystallised ruthenium.

Fused ruthenium has a specific gravity of 12·063 at 0°; like

[1] See Gutbier and Trenkner, *Zeit. anorg. Chem.*, 1905, **45**, 166.

iridium, it is hard and brittle, and next to osmium is the most infusible metal of the group. It can, however, be fused in the oxy-hydrogen flame[1] and distilled in the electric furnace.[2] With the exception of osmium, it is also the one which combines most readily with oxygen, the fused metal becoming covered with a brown film in the air, and on cooling it "spits" like silver and iridium. When heated in a current of oxygen it yields the dioxide, and at temperatures of about 1000° some tetroxide also is formed, although this substance decomposes when heated by itself at 107°.[3] The pure metal is scarcely attacked even by aqua regia, but it combines with chlorine at a red heat.

RUTHENIUM COMPOUNDS.

Ruthenium and Oxygen.

606 Ruthenium forms the oxides Ru_2O_3, RuO_2, and RuO_4, and, in addition, salts corresponding to the acidic oxides RuO_3 and Ru_2O_7 have been prepared. Oxides of the formulæ RuO, Ru_2O_5, and Ru_4O_9 have also been described, but, according to Gutbier and Ransohoff,[4] these do not exist.

Ruthenium Sesquioxide, Ru_2O_3. — When finely divided ruthenium is heated in the air it combines with 27 per cent. of its weight of oxygen, forming a blue powder which is insoluble in acids. This was regarded by Claus as the sesquioxide, but is more probably a mixture of the dioxide and metal (Gutbier and Ransohoff). The sesquioxide can be obtained, containing a trace of alkali, by heating the trihydroxide in dry carbon dioxide, and forms a black, scaly mass.

Ruthenium Trihydroxide, $Ru(OH)_3$, is obtained by precipitating the corresponding chloride with an alkali. It forms a blackish-brown precipitate, which even after washing with very dilute hydrochloric acid retains a trace of alkali. It dissolves with a yellow colour in acids, but is insoluble in water and alkalis.

The chief ruthenium salts are derived from the sesquioxide, and of these only a few of the halogen compounds are well known. The chloride and its double salts dissolve in water, forming

[1] Mylius and Dietz, *Ber.*, 1898, **31**, 3187.
[2] Moissan, *Compt. rend.*, 1906, **142**, 189.
[3] Debray and Joly, *Compt. rend.*, 1888, **106**, 100.
[4] *Zeit. anorg. Chem.*, 1905, **45**, 243, where the literature is quoted.

reddish-yellow solutions, which deposit on standing, slowly in the cold but quickly when warmed, a black, very finely divided precipitate of oxychloride. This reaction is so delicate that one part of the metal imparts a distinct ink-like colour to 100,000 parts of water.

Ruthenium Dioxide, RuO_2.—This oxide is obtained by roasting the disulphide or sulphate in contact with air. It is likewise formed when the metal is fused in an oxidising atmosphere, when it burns with a sparkling smoky flame, and evolves an ozone-like smell. Hence this compound can be easily obtained from the ruthenium contained in the osmiridium alloy, which may for this purpose be heated in a porcelain tube to the melting point of copper, in a current of pure air, from which all organic substance has previously been carefully separated. The ruthenium dioxide is carried forward by the osmium tetroxide formed at the same time, and deposited in the cold part of the tube, whilst the more volatile osmium compound is carried on still further by the current of air. Ruthenium dioxide crystallises in small, very hard, tetragonal pyramids, possessing a green metallic lustre, and a bluish or greenish iridescence. These have a specific gravity of 7·2, and are isomorphous with cassiterite and rutile (Rammelsberg).

Ruthenium Tetrahydroxide, $Ru(OH)_4,3H_2O$, is obtained, according to Claus, by evaporating ruthenium disulphate with caustic potash, when a dark-red precipitate falls down. The product always contains alkali, and has not been obtained pure. It dries to a reddish-brown mass, giving off water at 300°. When more strongly heated it deflagrates with vivid incandescence and evolution of a black, soot-like smoke. It is soluble in acids and alkalis, yielding yellow solutions.

Neither the oxides RuO_3 and Ru_2O_7 nor the corresponding acids have been prepared, but salts are known corresponding to these.

Potassium Ruthenate, K_2RuO_4,H_2O, is obtained by igniting a mixture of ruthenium, caustic potash, and potassium nitrate or carbonate, or by the action of 50 grams of the tetroxide on a solution of 70 grams of caustic potash in 500 c.c. of water at 60°; it crystallises from water in rhombic crystals having the above composition, which have a green metallic reflex, and are red in transmitted light. They take up moisture and carbon dioxide from the air and lose all their water at 200°.

Potassium per-ruthenate, $KRuO_4,H_2O$, is prepared by the action

of chlorine on a solution of the foregoing salt, or by dissolving 60 grams of caustic potash in 250 c.c. of water, warming to 60°, and adding 50 grams of ruthenium tetroxide previously fused under water. It forms black, lustrous, tetragonal octahedra. When heated in a vacuum at 400° it decomposes with formation of oxygen, ruthenium dioxide, and the ruthenate, or possibly a salt of potassium with a lower oxide.[1]

Ruthenium Tetroxide, RuO_4.—This compound, as already stated, is formed in small quantity when the metal is heated at 1000° in a current of oxygen, although when heated alone it decomposes at 106–107°. It is prepared by passing chlorine into a solution of potassium nitrosochlororuthenate, or of potassium ruthenate or sodium ruthenate prepared by fusing the metal with sodium peroxide; the liquid becomes heated and the tetroxide distils over and is deposited in the receiver. It is best purified by distillation through anhydrous calcium chloride in a vacuum, the apparatus employed being carefully freed from organic matter. It melts at 25·5°, the liquid readily remaining superfused, and solidifying to a vitreous mass. When heated it does not boil at 106°, but decomposes at 106–107° with a smoky flame but no explosion, the crystalline dioxide being formed. It may, however, be volatilised under reduced pressure, having a vapour pressure of 20 mm. at 42°, and of 183 mm. at 100·8°.

The moist oxide quickly decomposes; in the dry state it is fairly stable, but it decomposes in sunlight with formation of lower oxides. It dissolves slowly in water, and the solution when it contains free chlorine or hypochlorous acid may be kept without alteration for some days if light be excluded, but when pure slowly deposits a black precipitate. The vapour has a yellow colour and an irritating odour resembling that of ozone or nitrous fumes. According to Gutbier and Ransohoff, it does not attack the mucous membrane, but cannot long be endured and may produce severe symptoms of poisoning; it blackens organic matter rapidly, and is immediately reduced by alcoholic potash with separation of finely divided metallic ruthenium.[2] Serious explosions may occur if the solid tetroxide is treated with alcohol.

[1] Debray and Joly, *Compt. rend.*, 1888, **106**, 1494; 1891, **113**, 694.

[2] Debray and Joly, *Compt. rend.*, 1888, **106**, 328; Joly, *ibid.*, 1891, **113**, 693.

Ruthenium and the Halogens, Sulphur, and Nitrogen.

607 Only the trihalogen derivatives of ruthenium have been prepared in the pure state, but it is probable that dihalogen compounds are also formed, and numerous complex substances derived from the tetrahalogen series are known. When chlorine is passed over the metal, combination occurs slowly, but the resulting mass appears to be a mixture.

Ruthenium Dichloride, $RuCl_2$, has not been isolated, but is probably present in the blue liquid obtained by the action of sulphuretted hydrogen on a solution of the trichloride.

Ruthenium Trichloride, $RuCl_3$, is said to be formed when the finely divided metal is heated in a mixture of chlorine and carbonic oxide at 360–440° (Joly). It is best prepared by evaporating the tetroxide with hydrochloric acid, chlorine being evolved. It then forms a lustrous mass which dissolves readily in water, forming orange-yellow coloured solutions. The aqueous solution decomposes when gently warmed, an intensely black precipitate being produced (p. 1322).[1]

Double salts of the trichloride with alkali chlorides, R_2RuCl_5, known as *rutheniochlorides* or *chlororuthenites*, can easily be obtained,[2] the cæsium and rubidium compounds being the most characteristic and forming dark-coloured crystals containing $1H_2O$. According to Howe[3] an isomeric series of chlorides also exists which he terms the *aquochlororuthenates*. These salts are obtained by boiling the solutions of the rutheniochlorides with alcohol. *Potassium aquochlororuthenate*, $K_2Ru(OH_2)Cl_5$, crystallises in rose-red octahedra. Its solution is at once darkened by chlorine.

The trichloride unites with ammonia to form a compound, $2RuCl_3,7NH_3$, which forms a deep-red solution in water (Joly).

Ruthenium Tetrachloride, $RuCl_4$, is probably formed when the tetrahydroxide is dissolved in hydrochloric acid, but has not been obtained pure. Its compounds with the alkali chlorides and hydrochlorides of organic bases,[4] R_2RuCl_6, known as *ruthenichlorides* or *chlororuthenates*, can readily be obtained.

Potassium Ruthenichloride, K_2RuCl_6, is prepared by fusing

[1] Gutbier and Trenkner, *Zeit. anorg. Chem.*, 1905, **45**, 166.
[2] See Miolati and Tagiuri, *Gazz.*, 1900, **30**, ii, 511.
[3] *J. Amer. Chem. Soc.*, 1901, **23**, 775; 1904, **26**, 543.
[4] Gutbier and Zwicker, *Ber.*, 1907, **40**, 690.

ruthenium with potash and potassium chlorate, dissolving in cold water and adding dilute hydrochloric acid. It forms minute reddish-brown crystals and is sparingly soluble in cold water.[1] The salt formed by the action of chlorine on potassium aquochlororuthenate appears to be isomeric with this (Howe).

Ruthenium Oxychloride, RuO_2Cl_2, is not known, but double alkali salts, such as $RuO_2Cl_2,2CsCl$, have been prepared by the action of hydrochloric acid on the tetroxide in presence of an alkali chloride (Howe).

Ruthenium forms also a tribromide and a tri-iodide, and yields series of rutheniobromides and ruthenibromides which closely resemble the chlorine derivatives.[2]

A ruthenium trichloride and tetrachloride and double salts of these with alkali chlorides were described by Claus, but later investigation [3] has shown that these all contain nitrogen, and are in reality nitroso-derivatives.

Ruthenium Sulphide, Ru_2S_3.—This compound occurs as the mineral laurite, which is found with platinum ore in Borneo and Oregon, and usually contains a small percentage of osmium. It crystallises in small octahedra, generally showing also cube faces. Sulphuretted hydrogen gives a precipitate with solutions of ruthenium salts, which consists of a varying mixture of sulphides and oxysulphides of ruthenium with free sulphur.

According to Antony and Lucchesi [4] the precipitate produced in a solution of potassium ruthenichloride, K_2RuCl_6, at 0° is a mixture of the *trisulphide*, RuS_3, and sulphur, whilst at 80° the *disulphide*, RuS_2, is formed. These sulphides become incandescent or explode when gently heated in air.

Ruthenium Sesquisulphite, $Ru_2(SO_3)_3$.—When sulphur dioxide is slowly passed into a solution of ruthenic sulphate, $Ru(SO_4)_2$, the colour changes from bright red through green to blue. Alcohol added to this blue solution produces a blue precipitate of the colloidal sulphite, which may be dried at 80°. It dissolves in water and is precipitated by salts.[5]

Ruthenium Dithionate, RuS_2O_6, is obtained by the continued action of sulphur dioxide on a solution of ruthenic sulphate, and

[1] Antony and Lucchesi, *Gazz.*, 1899, **29**, ii, 82.

[2] Gutbier and Trenkner, *Zeit. anorg. Chem.*, 1905, **45**, 178; Howe, *J. Amer. Chem. Soc.*, 1904, **26**, 942.

[3] Joly, *Compt. rend.*, 1888, **107**, 994; Howe, *Amer. Chem. J.*, 1894, **16**, 388.

[4] *Gazz.*, 1900, **30**, ii, 539.

[5] Antony and Lucchesi, *Gazz.*, 1900, **30**, ii, 71.

forms a yellow, crystalline, fibrous mass which is readily soluble in water.[1]

Ruthenic Sulphate, $Ru(SO_4)_2$, is obtained by dissolving the precipitated sulphide in nitric acid, or the tetrahydroxide in sulphuric acid; the reddish-yellow solution leaves on evaporation a yellowish-brown, amorphous mass, which yields a deliquescent powder closely resembling mosaic gold.

Ruthenium and Nitrogen.—When brown ruthenium sesquioxide is dissolved in nitric acid it forms a red nitrate; the latter on boiling with successive quantities of hydrochloric acid and evaporation at 120° yields a red, crystalline mass of *ruthenium nitrosochloride*, $RuCl_3NO,H_2O$; on recrystallisation from hot water this forms dichroic triclinic prisms having the composition $RuCl_3NO,5H_2O$, which rapidly effloresce in dry air. It may also be prepared by the action of aqua regia on the tetroxide.[2] This substance combines with alkali chlorides forming double salts, which are identical with the substances formerly supposed to be double salts of ruthenium trichloride and the alkali chlorides.[3] The potassium salt has the composition $K_2[RuCl_5(NO)]$, and forms a violet-brown, iridescent powder consisting of orange-red, microscopic cubes. In aqueous solution it yields the ions K, K and $[RuCl_5(NO)]$, and it is dissociated to about the same extent as potassium platinichloride.[4]

The complex nitroso-derivatives have been investigated by Brizard.[5]

Ammoniacal Derivatives of Ruthenium.

608 Like most of the other members of this group, ruthenium forms a number of derivatives, the basic radical of which contains both ruthenium and ammonia. These were first examined by Claus, who described a series of salts derived from the hydroxide $Ru(NH_3)_4(OH)_2$, and also obtained a hydroxide to which he assigned the composition $Ru(NH_3)_2(OH)_2$. According to Joly,[6] however, the salts containing four molecules of

[1] Antony and Lucchesi, *Gazz.*, 1898, **28**, ii, 139.
[2] Howe, *J. Amer. Chem. Soc.*, 1894, **16**, 388.
[3] Joly, *Compt. rend.*, 1888, **107**, 994; 1889, **108**, 1300.
[4] Lind, *J. Amer. Chem. Soc.*, 1903, **25**, 928.
[5] *Compt. rend.*, 1899, **129**, 216; *Ann. Chim. Phys.*, 1900, [7], **21**, 311.
[6] *Compt. rend.*, 1889, **108**, 1300; 1890, **111**, 969; 1893, **115**, 1299; Howe, *J. Amer. Chem. Soc.*, 1894, **16**, 388.

ammonia also contain the nitroso-group, and have the general formula $Ru(NH_3)_4(NO)(OH)X_2$, where X is a halogen or monovalent acid radical, whilst the hydroxide containing two molecules of ammonia has the composition $Ru(NH_3)NO(OH)_3,H_2O$. The salts of the first-named series are well crystallised substances which usually have a golden-yellow colour, but no crystalline salts have been prepared from the second hydroxide. This view has been confirmed by Werner,[1] who regards these compounds as *hydroxynitrosotetrammineruthenium salts*, $[Ru(OH)(NO)(NH_3)_4]X_2$, derived from tetravalent ruthenium, and has prepared series of salts in which the hydroxyl group of the complex radical is replaced by chlorine, bromine, or water, the formula of this last series being $[Ru(H_2O)(NO)(NH_3)_4]X_3$.

Ruthenium and Carbon and Silicon.

609 *Rutheniocyanides.*—These compounds correspond to the ferrocyanides; the *potassium* salt, $K_4[RuCy_6],3H_2O$, is obtained by heating potassium ruthenio-nitrosochloride with potassium cyanide, and forms colourless crystals isomorphous with those of potassium ferrocyanide. Its solution is turned a dark violet colour by ferric salts, and yields a pale green precipitate changing to violet with ferrous salts, whilst the salts of mercury, lead, and zinc yield white precipitates.[2] The free *rutheniocyanic acid*, H_4RuCy_6, is prepared from the potassium salt by adding hydrochloric acid and extracting with ether, and crystallises in pearly laminæ readily soluble in water and alcohol. The solution has an acid reaction and an astringent taste, and on exposure to air assumes a blue colour (Claus).

Ruthenium Silicide, RuSi, is formed in small, white crystals when the elements are heated together in the electric furnace. It has the specific gravity 5·40, and is very hard. It is not attacked by boiling acids, but is decomposed by the halogens, burns when strongly heated in oxygen, and yields a per-ruthenate when fused with potassium hydrogen sulphate and potassium nitrate.[3]

[1] *Ber.*, 1907, **40**, 2614.

[2] See Howe, *J. Amer. Chem. Soc.*, 1896, **18**, 981; Howe and Campbell, *ibid.*, 1898, **20**, 29.

[3] Moissan and Manchot, *Compt. rend.*, 1903, **137**, 229.

Detection and Estimation of Ruthenium.

610 The ruthenic salts give a dark-red precipitate with concentrated solutions of potassium chloride and ammonium chloride, and on boiling with water the characteristic ruthenium oxychloride is formed. Ruthenium solutions are first coloured blue by sulphuretted hydrogen, and afterwards the brown sulphide is formed, which is almost insoluble in ammonium sulphide. The production of the volatile tetroxide is also a characteristic reaction.

Ruthenium, like the other members of this group, is estimated quantitatively as the metal.

Atomic Weight of Ruthenium.—Claus[1] first determined this constant, but the later investigations of Joly[2] with carefully purified material have shown that the figures of Claus are too high. Joly determined the atomic weight (1) by reducing the dioxide in hydrogen; (2) by the reduction of the nitrosochloride in hydrogen; (3) by the reduction of ammonium nitrosochlororuthenate, the numbers obtained being respectively 101·67, 101·74, and 101·62, and the atomic weight is therefore at present (1913) taken as 101·7.

RHODIUM. Rh = 102·9.

611 When Wollaston[3] in 1804 first acknowledged that he was the discoverer of palladium (p. 1336), he likewise intimated that he had found another new metal in platinum ore, to which he gave the name of rhodium, because the solutions of its salt possess a rose-red colour (*ῥόδον*, a rose). After Wollaston's time the metal and its compounds were investigated by Berzelius and Claus. In addition to its occurrence in platinum ore, rhodium has been found, according to Del Rio, alloyed with gold as rhodium-gold.

In order to prepare rhodium from the mixed platinum metals, the solution is employed from which ammonium platinichloride has been precipitated. The metals still in solution are then precipitated by metallic iron, and, according to the process of Deville and Debray, the metallic precipitate is fused with

[1] *Petersb. Akad. Bull.*, 3, 353.
[2] Joly, *Compt. rend.*, 1889, **108**, 946.
[3] *Phil. Trans.*, 1804, **94**, 419.

one part of lead and two parts of litharge. A regulus is thus obtained, from which the lead, copper, and palladium may be dissolved out by the action of dilute nitric acid. The insoluble metallic powder is then well mixed with five parts of barium peroxide and heated to redness for two hours, the solid mass being lixiviated with water, and the residue boiled with aqua regia in order to volatilise the osmium tetroxide, this latter being condensed. The excess of barium is precipitated from the solution by sulphuric acid, the filtrate evaporated at 100° with an excess of ammonium chloride, and the residue washed with a solution of the same salt as long as the wash-water has a rose-red colour. The filtrate is then evaporated with an excess of nitric acid in order to decompose the ammonium chloride, and the residual mass heated to redness with from three to four parts of sulphur. It is then rapidly boiled out with aqua regia and sulphuric acid, and by this treatment nearly pure rhodium remains behind. In order further to purify this it is fused with from three to four parts of zinc, and the alloy treated with strong hydrochloric acid, when the compound $RhZn_2$ remains behind. This is dissolved in aqua regia and evaporated with an excess of ammonia. Rhodammonium chloride, $Rh(NH_3)_5Cl_3$, separates out, and this is then purified from traces of iridium by recrystallisation, and ignited in a carbon crucible with some sulphur, and, lastly, in order to remove from it any traces of silicon and osmium, fused in the oxy-hydrogen or electric furnace.

Another method of preparing the pure metal is that described by Bunsen,[1] for the particulars of which his memoir on the subject must be consulted. He obtained from one kilogram of the platinum residues from the St. Petersburg mint 33·2 grams of pure rhodium sodium sulphate, $Na_3Rh(SO_4)_3$.

Commercial rhodium frequently contains iridium. If, however, the metals are converted into the chloropentammine chlorides, the rhodium salt may be obtained quite free from iridium by treating the mixture with nitric acid, filtering off the chloropentamminerhodium nitrate which crystallises out, and reconverting this into the chloride, which then yields rhodium quite free from iridium.[2]

Rhodium can also be obtained free from iridium, when the

[1] *Phil. Mag.*, 1868, [4], **36**, 253.

[2] Jörgensen, *Zeit. anorg. Chem.*, 1903, **34**, 82; see also Mylius and Dietz, *Ber.*, 1898, **31**, 3187; Leidié, *Compt. rend.*, 1900, **131**, 888; Leidié and Quennessen, *Bull. Soc. chim.*, 1901, [3], **25**, 840.

latter is present as an iridic salt such as $Ir(SO_4)_2$, by precipitating the mixed salts with caustic potash, dissolving the hydroxides in dilute sulphuric acid, and adding cæsium sulphate. The sparingly soluble rhodium cæsium alum separates in the cold, and can readily be purified by recrystallisation and then decomposed electrolytically.[1]

Properties.—Rhodium possesses the colour and lustre of aluminium, and has a specific gravity of 12·1. It fuses with greater difficulty than platinum, and spits on cooling, the surface becoming coloured blue from oxidation; it can be distilled in the electric furnace.[2] When a solution of one of its salts is heated with sodium formate, the metal is precipitated in the form of a fine black powder, possessing the property of decomposing formic acid, CH_2O_2, with evolution of heat, into hydrogen and carbon dioxide. After a time the action becomes weaker, but the powder then simply requires to be washed with water and dried in the air to be again rendered active. At a somewhat higher temperature, and in presence of caustic potash, it also decomposes alcohol, C_2H_5OH, with evolution of hydrogen and formation of potassium acetate, $CH_3{\cdot}CO_2K$; it does not lose this power at a temperature at which glass begins to soften (Deville and Debray). An unstable, colloidal solution of rhodium can be obtained by reducing the pure chloride with hydrazine hydrate. In presence of gum arabic the solution can be evaporated over sulphuric acid and yields a dark brown residue which contains 99·4 per cent. of rhodium and is almost completely soluble in warm water.[3] Pure rhodium, as well as that which contains gold and platinum, is almost insoluble in acids. If, however, it be alloyed with bismuth, zinc, lead, or copper, it dissolves in aqua regia. Alloys of much platinum and little rhodium also dissolve in aqua regia, but if the rhodium be present in larger quantity much remains undissolved. Rhodium can, however, be brought into solution by repeated ignition with fused potassium hydrogen sulphate, as well as with phosphoric acid or acid phosphates. Of all the platinum metals rhodium is the most easily attacked by chlorine. Rhodium combines with tin, yielding the alloy $RhSn_3$, which forms small brilliant crystals.[4] It forms also a

[1] Piccini and Marino, *Zeit. anorg. Chem.*, 1901, **27**, 62.
[2] Moissan, *Compt. rend.*, 1906, **142**, 189.
[3] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 452.
[4] Debray, *Compt. rend.*, 1887, **104**, 1470.

bismuth compound, $RhBi_4$, which crystallises in needles and is completely soluble in aqua regia;[1] it appears to form a compound with gold, but not with silver.

Finely divided rhodium absorbs very little hydrogen, but acts as a catalyst in bringing about the union of hydrogen and oxygen in a similar manner to platinum black.[2]

Crucibles and other forms of chemical apparatus are now made of malleable rhodium, and it is essential to use the perfectly pure metal for their preparation (Matthey).

RHODIUM COMPOUNDS.

Rhodium and Oxygen.

612 Rhodium forms three oxides, having the formulæ RhO, Rh_2O_3, and RhO_2.

Rhodium Monoxide, RhO, is obtained by heating the trihydroxide, $Rh(OH)_3$, by the cupellation of an alloy of rhodium and lead, or by igniting the finely divided metal in a current of air. It is a grey powder, with metallic appearance, which is not attacked by acids, and when heated in hydrogen is reduced with evolution of light.

Rhodium Sesquioxide, Rh_2O_3, is obtained as a grey, iridescent, spongy mass by heating the nitrate. It is also formed as a crystalline mass when sodium rhodochloride is heated in oxygen. It is perfectly insoluble in acids.

Rhodium Trihydroxide, $Rh(OH)_3$, is a black, gelatinous precipitate, obtained by heating a solution of sodium rhodochloride with excess of caustic potash. On drying it forms a heavy, dark brown mass having a conchoidal fracture and a metallic lustre. It is scarcely attacked by acids, hydrochloric acid dissolving it but very slightly.

If a solution of the sodium double chloride be treated in the cold with potash not in excess, it becomes opaque, and on long standing deposits thin, lemon-yellow crystals of the hydroxide, $Rh(OH)_3,H_2O$, which dissolve readily in acids, and, when moist, in caustic potash. When chlorine is passed into the solution of the yellow hydroxide in caustic potash, a blue coloration

[1] Rössler, *Chem. Zeit.*, 1900, **24**, 733.

[2] Quennessen, *Compt. rend.*, 1904, **139**, 795; *Bull. Soc. chim.*, 1905, [3], **33**, 191.

is produced,[1] which is probably due to the formation of a per-rhodate, Na_2RhO_4.

The rhodium salts are derived from the sesquioxide. They possess either a dark-red or a yellow colour, and have a bitter but not astringent taste.

Rhodium Dioxide, RhO_2, is obtained by repeated fusion of the metal with caustic potash and saltpetre. The sesquioxide is first formed, and this undergoes further oxidation. It closely resembles the sesquioxide; it is attacked neither by alkalis nor by acids, and is reduced by hydrogen only at a high temperature.

Rhodium Tetrahydroxide, $Rh(OH)_4$.—When chlorine is passed into the alkaline solution of the sesquihydroxide for a long time, and caustic potash occasionally added, this compound separates out as a green powder, the liquid becoming coloured blue or violet. The green powder dissolves in hydrochloric acid, yielding a blue solution, and this colour gradually changes to dark-red, chlorine being evolved. The violet-blue solution probably contains the potassium salt of a rhodous acid, which latter separates out after some time as a blue powder, gas being simultaneously evolved. On drying, it is converted into the tetrahydroxide.

Insoluble crystalline salts of the composition $K_2O,6RhO_2$, $Na_2O,8RhO_2$, and $BaO,12RhO_2$ are obtained when the corresponding double nitrites are heated in vacuo and the products treated with water. These substances may be regarded as *rhodites*, analogous to the manganites, cobaltites and chromites.[2]

Rhodium Salts.

613 *Rhodium Trichloride*, $RhCl_3$, is obtained by the continued ignition of the finely divided metal in chlorine, and also by heating one of the alkali double salts with sulphuric acid, and pouring the cooled mixture into water; a rose-red powder of insoluble rhodium chloride remains behind. It may be conveniently prepared from the crude double chloride, $RhCl_3,3NaCl$, obtained by the action of chlorine on the metal in presence of sodium chloride, by dissolving it in water, precipitating the sodium chloride by hydrochloric acid, evaporating, and heating the residue in a current of chlorine or hydrogen chloride. It then forms a brown powder, insoluble in water or acids, but

[1] See Alvarez, *Compt. rend.*, 1905, **140**, 1341.

[2] Leidié, *Compt. rend.*, 1899, **129**, 1249.

soluble in alkalis and in potassium cyanide.[1] It is obtained also as a brick-red powder by heating the rhodium tin alloy, $RhSn_3$, in chlorine at 440°, the tin volatilising as stannic chloride. When the yellow hydroxide is dissolved in hydrochloric acid, a yellow solution is obtained possessing an astringent taste, which on concentration becomes rose-red, and then possesses the peculiar bitter taste characteristic of all rhodium salts. When this solution is evaporated, a dark-red, amorphous mass of the hydrated chloride is obtained, which is deliquescent, and on further heating yields the insoluble anhydrous chloride.

The trichloride yields a large number of well-crystallised *rhodochlorides* or *chlororhodites*. The *sodium* salt, $Na_3RhCl_6,9H_2O$, crystallises in deep cherry-red, triclinic prisms, which are very soluble in water, and effloresce in the air to a peach-blossom coloured powder. The *ammonium* salt, $2(NH_4)_3RhCl_6,3H_2O$, forms four-sided, rhombic prisms.

The dark salt formed with potassium chloride has the formula $2KCl,RhCl_3$ or K_2RhCl_5. It crystallises in dark-red, acicular prisms which contain $1H_2O$, according to Berzelius, but according to Leidié are anhydrous. Another hydrate, $K_2RhCl_5,3H_2O$, crystallising in dark-red prisms has been described by Claus.

Rhodium Monosulphide, RhS.—When rhodium is heated in sulphur vapour it takes fire with formation of the sulphide, which is produced also when sulphuretted hydrogen is passed through a solution of a rhodium salt, and the washed precipitate dried by ignition in a current of carbon dioxide. Thus obtained, it forms a bluish-white fused mass having a metallic lustre, and, when heated in the air, leaves a residue of spongy rhodium.

Rhodium Sesquisulphide, Rh_2S_3, is obtained in the pure state by heating the trichloride in sulphuretted hydrogen at 360°, and forms blackish, crystalline plates. The *hydrosulphide*, $Rh(SH)_3$, is precipitated when sulphuretted hydrogen in large excess is passed into a solution of a rhodium salt at 100°, and forms a brownish-black precipitate which is insoluble in ammonium sulphide.[2]

Rhodium Sulphite, $Rh_2(SO_3)_3,6H_2O$, is obtained by dissolving the yellow hydroxide in sulphurous acid and evaporating. It is a pale yellow, indistinctly crystalline mass, and forms crystalline double salts.

[1] Joly and Leidié, *Compt. rend.*, 1898, **27**, 103.
[2] Leidié, *Compt. rend.*, 1888, **106**, 1533.

Rhodium Sulphate, $Rh_2(SO_4)_3,12H_2O$, is obtained by dissolving the yellow hydroxide in sulphuric acid, evaporating, and washing away the excess of acid by alcohol. It is a yellow, crystalline mass which possesses a sour astringent taste. The anhydrous salt is a brick-red, non-hygroscopic powder (Leidié). According to Claus it forms crystalline double salts with the alkali sulphates, but Leidié was unable to confirm this statement.

A series of *rhodium alums* of the alkali metals, ammonium, and thallium has been prepared by dissolving the yellow hydroxide in excess of dilute sulphuric acid and adding two-thirds of the calculated amount of the alkali sulphate.[1] *Rhodium cæsium alum*, $Cs_2SO_4,Rh_2(SO_4)_3,24H_2O$, forms yellow octahedra, melts at 110–111°, and is sparingly soluble in cold water. The potassium compound, on the other hand, is extremely soluble in water, the rubidium and ammonium salts being intermediate in solubility.

Rhodium Nitrite, $Rh(NO_2)_3$, has not been isolated, but forms characteristic double salts. *Sodium rhodium nitrite*, $3NaNO_2,Rh(NO_2)_3$, separates in bulky white crystals, which act on polarised light. The *potassium* salt also forms white, microscopic crystals when pure,[2] but is usually obtained as a heavy, orange-coloured, crystalline powder, which dissolves readily in hydrochloric acid.

Rhodium Nitrate, $Rh(NO_3)_3$, does not crystallise, but forms a dark yellow, hygroscopic, gummy mass.

Potassium Rhodicyanide, $K_3[RhCy_6]$, is obtained in a similar way to the corresponding iridium salt (see p. 1368), which it closely resembles; it is distinguished from the latter inasmuch as acetic acid produces a pale crimson-red precipitate of rhodium cyanide, $RhCy_3$, which dissolves in the cyanides of the alkali metals, forming the rhodicyanides (Martius). It may also be prepared by dissolving the yellow hydroxide in caustic potash, diluting, and adding the solution to an excess of hydrocyanic acid.[3]

Ammoniacal Derivatives of Rhodium.

614 The ammoniacal rhodium bases and salts closely resemble the corresponding cobalt compounds. The three chief series have the following general formulæ:

[1] Piccini and Marino, *Zeit. anorg. Chem.*, 1901, **27**, 62.
[2] Leidié, *Compt. rend.*, 1890, **111**, 106.
[3] Leidié, *Compt. rend.*, 1900, **130**, 87.

Hexammine salts (Luteo-salts) $[Rh(NH_3)_6]X_3$
Aquopentammine salts (Roseo-salts) $[Rh(H_2O)(NH_3)_5]X_3$
Pentammine salts (Purpureo-salts) $[RhX(NH_3)_5]X_2$

in which X is a monovalent negative radical.

Hexammine-Rhodium Trichloride (*Luteorhodium Chloride*), $[Rh(NH_3)_6]Cl_3$, is obtained in colourless lustrous crystals by heating the salt next described with ammonia.

Chloropentammine-Rhodium Dichloride (*Chloropurpureorhodium Chloride*), $[RhCl(NH_3)_5]Cl_2$, is prepared by dissolving the alloy of rhodium and zinc in aqua regia and adding ammonia. It forms small yellowish lustrous rhombic crystals.

Aquopentammine-Rhodium Chloride (*Roseorhodium Chloride*), $[Rh(H_2O)(NH_3)_5]Cl_3,H_2O$, is obtained by digesting the foregoing compound with silver oxide for several days, and dissolving the resulting base in hydrochloric acid.

Optically Active Rhodium Ammine Salts.—There is considerable similarity between rhodium and cobalt salts. The triethylenediamine cobalt salts form optical isomerides, and Werner has succeeded in obtaining the optical isomerides of triethylenediaminerhodium salts.[1]

Detection and Estimation of Rhodium.

615 Solutions of this metal are precipitated by sulphuretted hydrogen, slowly in the cold, but more quickly when warmed. The brown sulphide is insoluble in ammonium sulphide. When a rhodium compound is heated in hydrogen the metal is obtained; this is insoluble in aqua regia, but can be obtained in solution when it is fused with acid potassium sulphate. The fused mass on treatment with water yields a red solution, from which the metal is precipitated as a black powder on addition of caustic potash and alcohol. It is also precipitated from acid solution by zinc and other metals.

Rhodium is estimated quantitatively as the metal.

Atomic Weight of Rhodium.—Jörgensen,[2] from the analysis of chloropentamminerhodium dichloride and of the analogous dibromide, obtained the number 103·1 and Seubert and Kobbe,[3] by the same method, the number 102·94. This figure has been confirmed by the later work of Hüttlinger and Dittmar.[4] The value now adopted (1913) is 102·9.

[1] *Ber.*, 1912, **45**, 1228.
[2] *J. pr. Chem.*, 1883, [2], **27**, 486.
[3] *Annalen*, 1891, **260**,314.
[4] *Sitzungsber. phys. med. Soz. Erlangen*, 1907, **39**, 1; 1909, **40**, 184.

PALLADIUM. Pd = 106·7.

616 In April, 1803, a printed notice [1] came into the hands of Chenevix, to the effect that a new metal, called Palladium, was to be sold at Forster's, of Gerrard Street, Soho. Chenevix,[2] believing that this was simply a fraud, bought the whole stock, and after investigating the question he came to the conclusion that the substance was not a new metal, but that it was a platinum amalgam of peculiar properties. Soon after the communication of Chenevix's paper to the Royal Society (May 13, 1803), an advertisement appeared in which a handsome reward was offered to any one who should prepare even a grain of this substance, either according to Chenevix's plan, or by any other method. No one succeeded in obtaining the reward, although several German chemists endeavoured to prepare the new substance. In 1804 Wollaston [3] declared that he was the discoverer of palladium, having taken this name from that of a new planet Pallas, discovered by Olbers in 1802. At the same time he described the process which he adopted in order to obtain the new metal from platinum ore.

Palladium occurs in a tolerably pure state with Brazilian platinum ore, as well as together with gold, at Tilkerode, in the Harz. It is contained in most platinum ores, and is found in many places in South America alloyed with gold.

Numerous methods of separating palladium from the other platinum metals have been described. Among these may be mentioned the precipitation of the dicyanide by the addition of mercuric cyanide to a neutral solution of a palladium salt, and the treatment of the dichloride solution with potassium iodide,

[1] "Palladium, or new silver, has these properties amongst others that show it to be a new noble metal:—1. It dissolves in pure spirit of nitre, and makes a dark-red solution. 2. Green vitriol throws it down in the state of a regulus from this solution, as it always does gold from aqua regia. 3. If you evaporate the solution you get a red calx that dissolves in spirit of salt or other acids. 4. It is thrown down by quicksilver, and by all the metals but gold, platinum, and silver. 5. Its specific gravity by hammering was only 11·3; but by flattening as much as 11·8. 6. In a common fire the face of it tarnishes a little and turns blue, but comes bright again, like other noble metals, on being stronger heated. 7. The greatest heat of a blacksmith's fire would hardly melt it. 8. But if you touch it while hot with a small bit of sulphur, it runs as easily as zinc."

[2] *Phil. Trans.*, 1803, **93**, 290. [3] *Phil. Trans.*, 1804, **94**, 428; 1805, **95**, 316.

or freshly precipitated silver iodide,[1] which yields palladious iodide as a black insoluble precipitate. The cyanide is converted into the metal by ignition, and the iodide by heating in a current of hydrogen. Bunsen,[2] by the iodide method, prepared pure palladium from the platinum residues of the St. Petersburg mint, which consisted of a mixture of all the platinum metals. Other methods of working up the platinum metals on the large scale have been given by Philipp,[3] Guyard,[4] and Leidié.[5] From the palladium-gold alloy it may be obtained by fusing the latter with silver, and treating the granulated metal with moderately dilute nitric acid, which dissolves the silver and palladium, but leaves the gold unattacked. The silver is precipitated with sodium chloride, and the palladium from the filtrate by metallic zinc.[6]

To prepare pure palladium from the commercial metal, it is dissolved in aqua regia, and precipitated as the double ammonium chloride together with platinum and other metals. The precipitate is treated with excess of ammonia, when the palladium salt dissolves, and on addition of hydrochloric acid yields, after a time, a precipitate of yellow palladdiammonium chloride. This sometimes contains rhodammonium chloride, which is separated by retreatment with ammonia and addition of hydrochloric acid. The washed precipitate yields spongy palladium on ignition.

Palladium has a colour closely resembling that of silver and platinum, a specific gravity of 11·4 at 22·5° (Deville and Debray), or 11·9 (Mylius and Dietz);[7] it melts at 1549°, having the lowest melting point of all the platinum metals. At the melting point of iridium it boils violently, undergoing partial oxidation and emitting green vapours, which condense to a brown sublimate consisting of a mixture of oxide and metal.[8]

Palladium is dimorphous. The native metal occurs in the Brazils in the form of sand or rounded grains, amongst which small regular octahedra are sometimes found. Native palladium usually contains small quantities of both platinum and iridium, and has a specific gravity varying from 11·3 to 11·8. The

[1] Orloff, *Chem. Zeit.*, 1906, **30**, 714.
[2] *Phil. Mag.*, 1868, [4], **36**, 253.
[3] *Dingl. Polyt. Journ.*, 1876, **220**, 95.
[4] *Compt. rend.*, 1863, **56**, 1177.
[5] *Compt. rend.*, 1900, **131**, 888.
[6] Cock, *Phil. Mag.*, 1843, [3], **23**, 16.
[7] *Ber.*, 1898, **31**, 3187.
[8] See also Moissan, *Compt. rend.*, 1906, **142**, 189.

palladium found in the Harz occurs in small hexagonal tablets, together with gold and lead selenide, and hence this latter body was first considered to be palladium selenide. Owing to the difference of crystalline form this variety has been termed by Dana [1] *Allopalladium.*

When palladium is heated to dark redness it assumes a violet or blue colour, but at higher temperatures it regains its metallic lustre, and this remains even when the metal is quickly cooled by plunging into water. When heated in a current of oxygen till the weight is constant it forms the monoxide PdO.[2] Palladium dissolves readily in nitric acid, especially when this contains nitrous acid, or when the metal is alloyed with either copper or silver. Spongy palladium also dissolves in hydrochloric acid and in contact with the air, and the compact metal likewise dissolves in this acid if chlorine be passed into the liquid, and is attacked by boiling concentrated sulphuric acid, and by fused potassium bisulphate. Palladium readily absorbs hydrogen (p. 1340) and carbon monoxide,[3] and acts as a catalyst in many reactions.[4] When warm palladium foil is brought into an electrolytic mixture of hydrogen and oxygen, or other explosive gaseous mixture, combination takes place without explosion (Coquillon),[5] and when the metal is brought into the flame of alcohol or coal-gas it becomes covered with a thick film of soot. When palladium sponge is placed in a current of ethylene this gas is decomposed with separation of carbon, and this occurs at a temperature at which the gas alone does not undergo any alteration.[6] A colloidal solution of palladium can be prepared by the electrical method,[7] by the action of formaldehyde, hydrazine hydrate,[8] or carbon monoxide [9] on palladious chloride, and by the action of hydrazine hydrate or gaseous hydrogen on a palladium salt in presence of sodium protalbate.[10] This last preparation can be obtained by evaporation as a solid hydrosol, which absorbs hydrogen and

[1] *Mineralogy*, 5 ed. p. 12.

[2] Wilm, *Ber.*, 1892, **25**, 220; Wöhler, *Zeit. Elektrochem.*, 1905, **11**, 836.

[3] Harbeck and Lunge, *Zeit. anorg. Chem.*, 1898, **16**, 50.

[4] Lunge and Akunoff, *Zeit. anorg. Chem.*, 1900, **24**, 191; Zelinsky, *Ber.*, 1898, **31**, 3203.

[5] *Compt. rend.*, 1876, **83**, 709.

[6] Wöhler, *Annalen*, 1876, **184**, 128.

[7] Bredig and Fortner, *Ber.*, 1904, **37**, 798.

[8] Gutbier, *Zeit. anorg. Chem.*, 1902, **32**, 347; Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 358.

[9] Donau, *Monatsh.*, 1906, **27**, 71.

[10] Paal and Amberger, *Ber.*, 1904, **37**, 124; 1905, **38**, 1398.

dissolves readily in water. Colloidal palladium decomposes hydrogen peroxide and brings about the reduction of nitrobenzene to aniline by gaseous hydrogen.[1]

Palladium has not been employed very largely in the arts. For certain special purposes, however, it is useful; thus on account of its unalterability in the air, and owing to its bright silver-white colour, it has been employed for the preparation of graduated surfaces for astronomical instruments. It is likewise used for coating silver goods, as palladium does not lose its fine white colour on exposure to sulphuretted hydrogen, and hence it has also been much employed by dentists as a substitute for gold. Spongy palladium is used in gas analysis to absorb hydrogen.

It forms alloys with silver and copper.[2]

PALLADIUM COMPOUNDS.

Palladium and Oxygen.

617 Until recently only two oxides of palladium were supposed to exist,[3] viz., the monoxide, PdO, and the dioxide, PdO_2, but Wöhler and Martin have obtained a hydrated sesquioxide, Pd_2O_3,xH_2O.[4] A suboxide, Pd_2O, has also been described,[5] but it is probable that this is in reality a mixture of the metal and the monoxide (Wöhler and König).

Palladium Monoxide, PdO, is formed by the long-continued heating of the spongy metal in a current of oxygen at temperatures rising from 700–840°, or by heating a mixture of a palladium salt with potassium carbonate. Prepared in the first manner it is a bluish-green, and by the second an amber-coloured mass, which yields a black powder. On strong ignition it yields the metal, the dissociation pressure[6] being 760 mm. at 877°, and it is reduced by hydrogen at the ordinary temperature with evolution of light and heat. It acts as a powerful oxidising agent to organic substances, and is reduced to metal by

[1] Paal and Amberger, *Ber.*, 1905, **38**, 1406.
[2] Ruer, *Zeit. anorg. Chem.*, 1906, **51**, 223, 315.
[3] Wöhler and König, *Zeit. anorg. Chem.*, 1905, **46**, 323.
[4] *Zeit. anorg. Chem.*, 1908, **57**, 398.
[5] Kane, *Phil. Trans.*, 1842, **132**, 276; Neumann, *Monatsh.*, 1892, **13**, 40.
[6] Wöhler, *Zeit. Elektrochem.*, 1905, **11**, 836; 1906, **12**, 781.

hydrogen peroxide. If a palladious salt be precipitated with sodium carbonate, a dark-brown hydroxide, readily soluble in acids, is thrown down, whilst the anhydrous oxide dissolves only after long boiling. When precipitated in the cold it is soluble in alkalis, but loses this property when dried or when prepared from a boiling solution. The pure hydrated oxide is best prepared by the hydrolysis of the nitrate.

The palladious salts, corresponding to this oxide, possess a green, red, or brown colour, and have an astringent, but not metallic, taste.

Palladium Sesquioxide is obtained in the hydrated condition by the electrolytic oxidation of palladious nitrate. It forms a brown precipitate which dissolves readily in hydrochloric acid, forming an unstable chloride. Palladium is thus brought more into line with its neighbours rhodium and ruthenium.

Palladium Dioxide is obtained in an impure hydrated form as a brown precipitate by the addition of caustic soda to potassium palladichloride. This is soluble in acids, but becomes less soluble when preserved. It can be obtained free from alkali and basic salts by the anodic oxidation of the nitrate, but is not quite free from monoxide. The dioxide very readily decomposes into the monoxide and oxygen, and cannot be obtained in the anhydrous state. It acts as a vigorous oxidising agent, and decomposes hydrogen peroxide (Wöhler and König).

Palladium and Hydrogen.

618 *Palladium-Hydrogen.*—The absorption of hydrogen by palladium was discovered by Graham, who observed that it occurred when hydrogen was passed over metallic palladium which had been heated to redness, or when the metal was employed as the negative electrode in the electrolysis of water.[1]

The conditions of absorption and the nature of the change which occurs have already been discussed in Vol. I. pp. 157–161, and more recent investigations have not led to any definite conclusion.[2]

The product containing hydrogen often becomes heated on

[1] *Phil. Mag.*, 1866, **32**, 516.

[2] Hemptinne, *Zeit. physikal. Chem.*, 1899, **27**, 429; Shields, *Proc. Roy. Soc. Edin.*, 1898, **22**, 169; Winkelmann, *Ann. Physik*, 1901, [4], **6**, 104; 1905, [4], **16**, 773; Schmidt, *ibid.*, 1904, [4], **13**, 747; Paal and Amberger, *Ber.*, 1905, **38**, 1394, 2414; Richardson, *Proc. Phil. Soc. Camb.*, 1905, **13**, 27; Fischer, *Ann. Physik*, 1906, [4], **20**, 503.

exposure to the air from absorption of oxygen and formation of water, and when palladium black has been employed this action may be sufficiently vigorous to render the powder pyrophoric (Paal and Amberger). Palladium foil charged with hydrogen acts as an excellent reducing agent, reducing ferric and ceric salts, ferricyanides and chromates, and may be employed for this purpose in quantitative analysis.[1]

Colloidal palladium readily absorbs hydrogen, and in this way colloidal palladium-hydrogen has been obtained both in the solid state and in solution (Paal and Amberger).

The specific gravity of palladium-hydrogen is less than that of the metal, hence expansion must occur in the formation of the compound. This expansion can be shown in several ways. One of the most striking is to fit two palladium wires horizontally through the edges of a thin electrolytic trough with parallel glass sides. The trough is then filled with acidulated water, placed in the focus of the oxy-hydrogen or electric light, and the image of the wires thrown on the screen. An electric current is now passed through the cell, when a singular bending of the palladium wire from which the hydrogen is evolved is noticed. If the current be reversed this wire first returns to its original horizontal position, and then bends to the opposite side, whilst the other wire is deflected in the former direction; the explanation of this double bending being that first one side, and then the other side of the wire becomes saturated with, or loses the hydrogen.[2]

If one side of a piece of palladium foil be saturated electrolytically with hydrogen, then taken out of the liquid, washed and dried, and afterwards ignited, it becomes so bent that it has almost the appearance of having been rolled up into a coil.

The arrangement shown in Fig. 199 is that proposed by Wöhler[3] for exhibiting the decomposition of palladium hydrogen by heat and the reabsorption of the hydrogen on cooling

The U-tube (*a*) dipping in boiling water contains the spongy palladium, over which a current of hydrogen is passed for half an hour from the cylindrical generator on the right of the figure. The water bath is then removed and the tube allowed to cool in the current of hydrogen. The stop-cock (*d*) is now shut, and

[1] Chapman, *Analyst*, 1904, **29**, 346.

[2] Poggendorff, *Ber.*, 1869, **2**, 74; see also Dewar, *Phil. Mag.*, 1887, [4], **47**, 334.

[3] *Annalen*, 1876, **184**, 128.

the tube (*a*) placed in communication with the tube (*b*). This latter dips in the cylinder and is bent up at the lower end into the tube (*c*). The tube (*a*) is next heated with a flame, when the cylinder soon becomes filled with hydrogen, and on allowing the spongy metal to cool, a rapid absorption of the hydrogen occurs. The experiment can, of course, be repeated as often as desired.

Palladium Salts.

619 *Palladious Chloride*, $PdCl_2$, is obtained by heating palladious sulphide, PdS, in dry chlorine, when it is obtained partly as

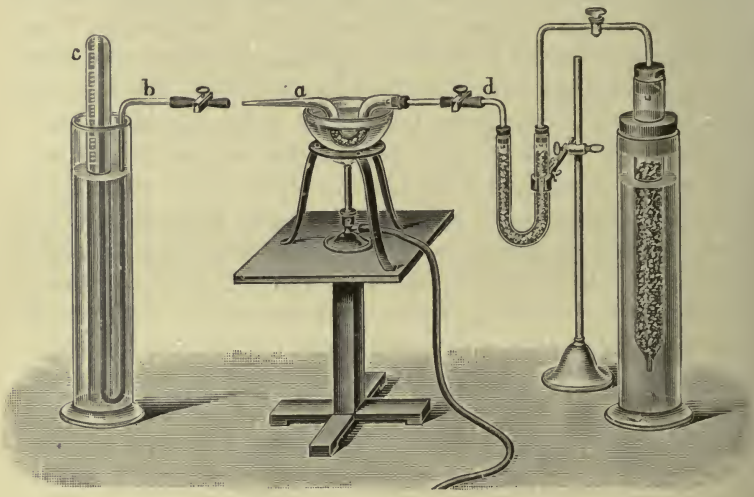


Fig. 199.

a rose-red sublimate and partly in the form of garnet-red crystal. which dissolve slowly but completely in water. It is prepared in solution by the simultaneous action of chlorine and hydrochloric acid on the metal. On evaporation over caustic lime, brown-red crystals, having the composition $PdCl_2,2H_2O$ are deposited. These lose water when gently heated, the anhydrous chloride remaining as a brownish-black mass which melts easily without decomposition, and is reduced by hydrogen in the cold. At a red-heat it fuses and loses half of its chlorine, forming the *monochloride*, PdCl, which, on cooling, solidifies to a reddish-brown crystalline mass yielding a light-red powder which is very deliquescent. The aqueous solution partially decomposes with separation of basic salts, and the solution is reduced by

hydrogen, carbon monoxide, and other gases.[1] When heated, palladious chloride unites with carbon monoxide,[2] forming the crystalline compounds, $PdCl_2,2CO$, melting at 142°, $2PdCl_2,3CO$, melting at 132°, and $PdCl_2,CO$. These substances are analogous to the corresponding platinum compounds.

Palladious chloride forms double chlorides with other chlorides, which are known as *palladiochlorides* or *chloropalladites*.[3] A very large number of these salts of organic bases have been prepared.[4]

Potassium Palladiochloride, K_2PdCl_4, is obtained by adding potassium chloride to a solution of palladious chloride. It may also be prepared by ignition of potassium palladichloride. It is easily soluble in water, less so in alcohol, and crystallises in four-sided prisms, which when viewed in the direction of the primary axis have a red, but in other directions exhibit a light-green, colour.

Ammonium Palladiochloride, $(NH_4)_2PdCl_4$, is obtained by evaporating a solution of palladium chloride with ammonium chloride. It forms either bronze-yellow prisms exhibiting a play of different colours, or yellowish-green needles, and dissolves in water, forming a dark-red solution.

Palladic Chloride, $PdCl_4$, is not known in the free state. The brown solution obtained by dissolving the metal in concentrated aqua regia contains *palladichloric* or *chloropalladic acid*, H_2PdCl_6, corresponding to platinichloric acid; this forms salts with the alkali metals and certain aromatic bases.[5]

Potassium Palladichloride, K_2PdCl_6, is obtained by adding potassium chloride to a solution of the metal in an excess of aqua regia and gently evaporating. It is also prepared by precipitating a solution of palladious chloride, saturated with chlorine, with an excess of potassium chloride. It forms cinnabar-red or brownish-red octahedra showing the faces of the cube. These dissolve in hot dilute hydrochloric acid without decomposition, but are not soluble in water containing the chlorides of the alkali metals, or in alcohol.

Ammonium Palladichloride, $(NH_4)_2PdCl_6$, is a bright-red

[1] Böttger, *J. pr. Chem.*, 1859, **76**, 233.

[2] Fink, *Compt. rend.*, 1898, **126**, 646.

[3] See Gutbier and Krell, *Ber.*, 1905, **38**, 2385.

[4] Gutbier, *Ber.*, 1905, **38**, 2105; *Zeit. anorg. Chem.*, 1905, **47**, 23; Gutbier and Krell, *Ber.*, 1905, **38**, 3869; 1906, **39**, 616, 1292; Gutbier and Woernle, *Ber.*, 1906, **39**, 2716.

[5] Möhlau, *Ber.*, 1906, **39**, 861.

crystalline powder, consisting of microscopic octahedra. It is obtained by precipitating a solution of the chloride, saturated with chlorine, by ammonium chloride. On treating the solution with an excess of ammonia a violent evolution of nitrogen takes place, ammonium palladiochloride being formed:

$$3(NH_4)_2PdCl_6 + 2NH_3 = 3(NH_4)_2PdCl_4 + 6HCl + N_2.$$

Palladious Bromide, $PdBr_2$, is obtained by treating the metal with bromine hydrate and nitric acid, and forms a chestnut-brown mass which dissolves in hydrobromic acid but not in water.

Potassium palladiobromide, K_2PdBr_4, crystallises in lustrous reddish-brown needles which are stable in the air. Many analogous salts are known (Gutbier and Krell).

Palladic Bromide, $PdBr_4$, is not known, but the *palladibromides* of the alkali metals, R_2PdBr_6, have been prepared by passing bromine vapour into the solutions of the corresponding palladiobromides. They are sparingly soluble salts which are decomposed by hot water and by ammonia (Gutbier and Krell).

Palladious Iodide, PdI_2, is obtained by precipitating the chloride with potassium iodide as a black flocculent precipitate which, when dried in the air, forms a deliquescent mass exhibiting a conchoidal fracture. It dissolves slowly in hydriodic acid and readily in a solution of potassium iodide, imparting to this a wine-red colour. When heated to 100° it begins to give off iodine, and it decomposes completely at temperatures between 330° and 360°. The solution in potassium iodide yields on evaporation blackish-green deliquescent cubes.

Palladium Subsulphide, Pd_2S, is obtained by fusing ammonium palladiochloride with sodium carbonate, sulphur, and ammonium chloride. A green molten mass is thus obtained which crystallises on cooling and exhibits a metallic fracture. It is only slowly attacked by aqua regia.

Palladium Monosulphide, PdS, is formed with incandescence when the metal is heated in the vapour of sulphur. It is a bluish-white hard mass, which exhibits a laminated fracture and a metallic lustre, and oxidises only slowly in the air. A black precipitate is formed by passing sulphuretted hydrogen through a solution of a palladious salt; this is generally supposed to be palladious sulphide, but according to Petrenko-Kritchenko[1] it always contains more sulphur than is required by the formula PdS.

[1] *Zeit. anorg. Chem.*, 1893, **4**, 247.

Palladium Disulphide, PdS_2.—When the foregoing compound is fused with sodium carbonate and sulphur, *sodium thiopalladate*, Na_2PdS_3, is formed. This crystallises in reddish-brown needles, having a slightly metallic lustre. It is decomposed by hydrochloric acid with formation of the disulphide, which is a crystalline dark-brown powder easily soluble in aqua regia. When heated in carbon dioxide it is first converted into the monosulphide, and at a higher temperature into the subsulphide.

A salt of the formula $(NH_4)_2PdS_{11},\frac{1}{2}H_2O$ crystallises slowly in slender yellowish-red needles when solutions of ammonium polysulphide and potassium palladiochloride are mixed.[1]

Sodium Palladiosulphite, $[Pd(SO_3)_4]Na_6,2H_2O$, is obtained as a white crystalline precipitate by adding caustic soda to a solution of the chloride which has been saturated with sulphur dioxide.

Palladious Sulphate, $PdSO_4,H_2O$, is obtained by dissolving the hydroxide in sulphuric acid, or by dissolving the metal in the same solvent with the addition of nitric acid. It forms indistinct olive-green deliquescent crystals which are decomposed by water with formation of a basic salt, $PdSO_4,7Pd(OH)_2$, as a brown insoluble powder.

Potassium Palladionitrite, $[Pd(NO_2)_4]K_2$, is obtained on addition of potassium nitrite to a hot solution of potassium palladiochloride as a pale-yellow crystalline powder, the production of which serves as a microchemical test for palladium.[2]

Numerous complex nitrites, sulphites, phosphates, and oxalates have also been described.[3]

Palladious Nitrate, $Pd(NO_3)_2$, is formed by dissolving the metal or the oxide in nitric acid. It crystallises in long brownish-yellow rhombic prisms which probably contain water of crystallisation, and are very deliquescent. A brown powder of $Pd(NO_3)_2,3Pd(OH)_2$ is formed on the addition of water to the solution.

Palladious Cyanide, $PdCy_2$, is obtained as a pale-yellow precipitate on addition of mercuric cyanide solution to a solution of palladious salt, which must contain no free acid and should not be too dilute. On solution in potassium cyanide

[1] Hofmann and Höchtlen, *Ber.*, 1904, **37**, 245.

[2] Pozzi-Escot and Couquet, *Compt. rend.*, 1900, **130**, 1073.

[3] Rosenheim and Itzig, *Zeit. anorg. Chem.*, 1900, **23**, 28; Vezes, *Bull. Soc. chim.*, 1899, [3], **21**, 172; Loiseleur, *Compt. rend.*, 1900, **131**, 262; Finck, *ibid.*, 1896, **123**, 603.

and evaporation, transparent thin rhombic prisms of *potassium palladiocyanide*, $K_2[PdCy_4],3H_2O$, or small tablets containing $1H_2O$ are obtained. The cyanide is also soluble in acids and in ammonia, and the latter solution yields *palladosammine cyanide*, $[Pd(NH_3)_2Cy_2]$, in needles or in crystalline scales possessing a pearly lustre.

Palladious Thiocyanate, $Pd(SCy)_2$ is a reddish flocculent precipitate, and dissolves in potassium thiocyanate solution forming *potassium palladiothiocyanate*, $K_2[Pd(SCy)_4]$, which crystallises in ruby-red needles.[1]

Ammoniacal Palladium Compounds.

620 These have been investigated chiefly by Hugo Müller,[2] and are formed by the action of ammonia on palladious salts.

They appear to belong to two series:

Palladosammine compounds, $[Pd(NH_3)_2X_2]$,
Palladodiammine compounds, $[Pd(NH_3)_4]X_2$,

and are analogous to the corresponding platinum compounds (p. 1399). Unstable hydroxylamine derivatives have also been prepared which probably belong to the same two series.[3]

An extended investigation of the palladosammine salts in which ammonia is replaced by organic nitrogen bases has been carried out by Gutbier and his colleagues.[4]

In addition to these, pyridine derivatives of the type $[Pd(NH_3)_2Cl_2]Cl_2$, derived from tetravalent palladium, have been described.[5]

Palladosammine Hydroxide, $[(OH)_2(NH_3)_2Pd]$, is obtained by the decomposition of the sulphate with baryta water, or of the chloride with silver oxide and water. The yellow solution thus obtained when dried over sulphuric acid yields a crystalline ochre-yellow mass. The solution has all the properties of a solution of an alkali hydroxide.

Dichloro-diammine Palladium or *Palladosammine Chloride* $[Cl_2(NH_3)_2Pd]$, is obtained by the addition of an excess of ammonia to palladious chloride and either evaporating, or,

[1] Bellucci, *Atti R. Accad. Lincei*, 1904, [5], **13**, ii, 386.

[2] *Annalen*, 1853, **86**, 341.

[3] Zeisel and Nowack, *Annalen*, 1907, **351**, 439.

[4] *Ber.*, 1905, **38**, 2107, 3869; 1906, **39**, 616, 1292, 2716; *Zeit. anorg. Chem.*, 1905, **47**, 23; see also Hardin, *J. Amer. Chem. Soc.*, 1899, **21**, 943.

[5] Rosenheim and Maas, *Zeit. anorg. Chem.*, 1898, **18**, 331.

better, precipitating the salt by means of hydrochloric acid. It forms fine yellow needles, which consist of glistening octahedra placed one upon the other, and is almost insoluble in water.

Tetramminepalladious Hydroxide or *Palladodiammine Hydroxide*, $[(NH_3)_4Pd](OH)_2$, is obtained by the decomposition of the sulphate with baryta water. It is a colourless crystalline mass, the aqueous solution of which has a strong alkaline reaction, precipitates the salts of copper, iron, cobalt, nickel, and aluminium, but not those of silver, and decomposes ammoniacal salts.

Tetramminepalladious Chloride or *Palladodiammine Chloride*, $[(NH_3)_4Pd]Cl_2$, is formed by the repeated evaporation of palladious chloride with ammonia. It crystallises in large, colourless, four-sided, monoclinic prisms, and is easily soluble in water.

The *double salt*, $[Pd(NH_3)_4]Cl_2,PdCl_2$, known as Vauquelin's salt, is obtained by the action of a slight excess of ammonia on palladious chloride.

Detection and Estimation of Palladium.

621 The two most characteristic reactions of palladium are (1) the precipitation of its hydrochloric acid solution by potassium cyanide, the yellowish-white palladium cyanide being thrown down, soluble in both hydrochloric acid and ammonia; and (2) the production of a black precipitate of palladious iodide, insoluble in hydrochloric acid, when potassium iodide or freshly precipitated silver iodide is added to a palladium solution. By these reactions it may be separated from all metals, with the exception of copper, and this may be previously removed, according to Wöhler, by precipitation as cuprous thiocyanate, after saturation with sulphur dioxide.

Palladium is estimated gravimetrically as the metal, obtained by the ignition of the cyanide or by the reduction of the salts with a hydrazine salt[1] in acid solution.[2] Palladium may be estimated also by precipitating with acetylene and igniting the precipitate,[3] and by weighing the metal deposited electrolytically with a rotating anode.[4]

[1] Jannasch and Bettges, *Ber.*, 1904, **37**, 2210.

[2] Jannasch and Rostosky, *Ber.*, 1904, **37**, 2441; Paal and Amberger, *Ber.*, 1905, **38**, 1388.

[3] Erdmann and Makowka, *Ber.*, 1904, **37**, 2694.

[4] Amberg, *Zeit. Elektrochem.*, 1904, **10**, 385.

Atomic Weight of Palladium.—Until the year 1889 the only determination of the atomic weight of palladium was that of Berzelius, who obtained the number 106 by the analysis of potassium palladiochloride. Since 1889 the atomic weight has been redetermined by several investigators, but the different results vary considerably. Keiser[1] by the determination of the palladium in palladosammine chloride found the number 106·5, and in a later determination by the same method, using very carefully purified material, Keiser and Breed[2] found the value 106·47. Bailey and Lamb[3] by the same method found the number 105·7, and a value closely agreeing with this, viz., 105·8, was obtained by Joly and Leidié[4] by the analysis of potassium palladiochloride. Keller and Smith,[5] on the other hand, from the electrolytic determination of the metal in palladosammine chloride obtained the much higher number 107·1.

A high figure, 106·99, was also obtained by Hardin[6] who estimated the metal in diphenylpalladodiammonium chloride, $Pd[NH_2(C_6H_5)Cl]_2$, and the corresponding bromide, and in ammonium palladiobromide. On the other hand, Amberg[7] has obtained a lower number, 106·64, by the analysis of palladosammine chloride, the chlorine and the metal being both estimated. Shinn[8] reduced the double chloride of palladium and ammonium with formic acid, and found as the mean atomic weight the figure 106·71. The most probable value is (1913) taken as 106·7.

SUB-GROUP (*c*). THE PLATINUM GROUP.

Osmium. Iridium. Platinum.

622 These metals are distinguished by their high specific gravity and melting point. Osmium alone forms a tetroxide, thus resembling ruthenium.

The tendency to form complex salts is exceedingly strongly marked, and with the exception of the sulphides and halogen derivatives, very few simple salts are known. Such as are

[1] *Amer. Chem. J.*, 1889, **11**, 398.
[2] *Amer. Chem. J.*, 1894, **16**, 20.
[3] *Journ. Chem. Soc.*, 1892, **61**, 745.
[4] *Compt. rend.*, 1893, **116**, 146.
[5] *Amer. J. Sci.*, 1892, **44**, 423.
[6] *J. Amer. Chem. Soc.*, 1899, **21**, 943.
[7] *Annalen*, 1905, **341**, 235.
[8] *J. Amer. Chem. Soc.*, 1912, **34**, 1448. Compare Gutbier, Hass, and Gebhardt, *J. pr. Chem.*, 1909, **79**, 457.

known have the general formulæ MR_2, MR_3, and MR_4, corresponding to the basic oxides MO, M_2O_3, and MO_2, but the series MR_3 is scarcely represented among the platinum compounds. The most important of the series of the complex salts are the halogen acids and their derivatives, such as K_2PtCl_4, K_3IrCl_6, and K_2OsCl_6, the complex nitrites, such as $K_3Ir(NO_2)_6$ and $K_2Pt(NO_2)_4$, the complex cyanides and thiocyanates, such as $K_2Pt(CN)_4$ and $K_2Pt(SCN)_4$, the sulphites, and above all the ammoniacal derivatives.

OSMIUM. Os = 190·9.

623 In 1803 Smithson Tennant investigated the metallic residue which remains when platinum ores are dissolved, and this he believed to contain a new metal. At the same time Descotils, as well as Fourcroy and Vauquelin, examined the same subject, and also came to the conclusion that the solution contained a peculiar metal. However, in 1804 Tennant[1] proved that the platinum residues contained two new metals, to one of which he gave the name of iridium, on account of the varying colour of its salts, and to the other the name osmium (*ὀσμή*, a smell), because of the peculiar odour which its volatile oxide possesses. Osmium is found in platinum ores in the form of an alloy with iridium, known as osmiridium, which is described under iridium (p. 1361). It may be easily separated from the other members of the platinum group by means of its property of combining directly with oxygen to form a very volatile tetroxide, OsO_4. This compound is obtained, in a more or less pure state, in the course of the preparation of the other platinum metals, and especially of ruthenium (see p. 1319). The solution thus obtained may be precipitated with ammonia and ammonium sulphide, and the precipitated sulphide mixed with sodium chloride, and heated in a slow current of chlorine. The mass when lixiviated yields sodium osmichloride, Na_2OsCl_6, and from this solution ammonium osmichloride is thrown down by ammonium chloride. This is next washed with ammonium chloride solution, and then heated in a covered crucible, when spongy osmium is obtained. The sulphide may also be simply heated in a well-covered carbon crucible to the temperature of the melting point of nickel.

[1] *Phil. Trans.*, 1804, **94**, 411.

Pure osmium was obtained by Deville and Debray,[1] by passing the vapour of the pure tetroxide mixed with carbon monoxide and carbon dioxide through a red-hot porcelain tube. Thus prepared, the metal assumes the form of an amorphous powder, which is converted into the crystalline variety when fused with from three to four times its weight of tin in a charcoal crucible, the crystalline alloy treated with hydrochloric acid, and the residue heated in a current of hydrogen chloride.

The crystalline form of osmium is either that of the cube or of a very obtuse rhombohedron. The crystals possess a bluish-white colour with violet lustre, are harder than glass, and possess a specific gravity of 22·477. Hence osmium is the heaviest of known bodies, and it is likewise one of the most infusible and least volatile of the metals. The melting point of the metal is about 2500°; it may be distilled at the highest temperature of the electric furnace, but the volatilisation takes place much more slowly than that of the other platinum metals.[2]

Osmium undergoes oxidation somewhat readily when finely divided, being oxidised and volatilised when heated in air below 212° and in oxygen below 170°, but not below 155°. When strongly heated in air oxidation of the compact metal also takes place, and this operation is attended with great danger owing to the formation of the highly poisonous tetroxide. Deville in this manner was rendered almost blind for twenty-four hours by having accidentally become exposed to the vapour of the tetroxide. This substance produces the most violent pain and inflammation of the conjunctiva, and vision is permanently injured by the subsequent reduction of a film of metallic osmium.[3]

Crystalline osmium is not attacked even by aqua regia, and must be brought into solution by fusion with sodium peroxide, caustic soda, and potassium nitrate, or barium peroxide and nitrate; the amorphous metal, on the other hand, is readily dissolved by fuming nitric acid, more slowly by aqua regia.

On account of its high melting point, osmium has been employed for the preparation of the filaments of incandescent electric lamps, but owing to its high cost tungsten is now more generally employed, and the alloy osmiridium, or osrid, which is not attacked by acids, is employed for tipping gold fountain

[1] *Compt. rend.*, 1876, **82**, 1076.
[2] Moissan, *Compt. rend.*, 1906, **142**, 189.
[3] *Ann. Chim. Phys.*, 1859, [3], **56**, 400.

pens, and, inasmuch as it is unoxidisable and non-magnetic, it has been employed for the bearings of the mariner's compass and watch bearings.

Colloidal Osmium.—The metal may be obtained in the colloidal condition by reducing potassium osmate with hydrazine hydrate in presence of sodium lysalbate or protalbate [1] or gum arabic,[2] and dialysing the product. This still contains oxygen, which is removed by heating in hydrogen at 30–40°, the residue being completely soluble in water. It effects the catalytic decomposition of hydrogen peroxide more rapidly than any of the other colloidal metals of this group.

COMPOUNDS OF OSMIUM.

Osmium and Oxygen.

624 The following oxides are known :

Osmium Monoxide,	OsO,
Osmium Sesquioxide,	Os_2O_3,
Osmium Dioxide,	OsO_2,
Osmium Tetroxide,	OsO_4.

In addition to these, osmic acid, H_2OsO_4, and its salts are known, but the corresponding oxide has not been prepared.

The first three of these oxides act as feeble basic oxides, but very few of their salts have as yet been examined, only the sulphite and chloride corresponding to the monoxide, and double chlorides of the formula $3M^{I}Cl,OsCl_3$, corresponding to the sesquioxide, being known. The chloride, $OsCl_4$ has, however, been prepared along with double chlorides corresponding to the derivatives of platinichloric acid. Osmic acid forms a series of osmates with the alkali metals, whilst the tetroxide yields a neutral solution in water, and forms salts with neither acids nor bases.

Osmium Monoxide, OsO, is obtained when the corresponding sulphite mixed with sodium carbonate is ignited in a current of carbon dioxide. It is a greyish-black powder insoluble in acids.

Osmium Sesquioxide, Os_2O_3, is a black powder, insoluble in acids, obtained by heating its salts with sodium carbonate in a

[1] Paal and Amberger, *Ber.*, 1907, **40**, 1392, 2201.
[2] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 452.

current of carbon dioxide. Deville and Debray obtained this oxide in copper-red scales, together with the metal, by the reduction of the tetroxide. A brownish-red *hydroxide* is precipitated by alkalis from solutions of the osmochlorides of the alkali metals.

Osmium Dioxide, OsO_2, is obtained from its salts in a similar way to the foregoing oxides. It is likewise formed when its hydroxide is heated in a current of carbon dioxide. Prepared in this way it forms masses having a coppery lustre. It does not decompose in absence of air even at a red-heat, but when mixed with combustible bodies it deflagrates on heating.

When caustic potash is added to a solution of potassium osmichloride, and when the aqueous solution of the tetroxide is mixed with alcohol or other reducing agent, or when potassium osmate is exposed to sunlight or treated with nitric acid, a black precipitate is obtained, which according to Claus and Jacoby[1] is *osmium tetrahydroxide*, $Os(OH)_4$. Moraht and Wischin,[2] however, find that this in reality consists of osmic acid, H_2OsO_4.

Osmium Trioxide, OsO_3, is unknown, but the corresponding *osmic acid*, H_2OsO_4, is stated by Moraht and Wischin to be produced in the manner just described. After drying over phosphoric oxide it forms a black powder, which oxidises in the air to the tetroxide, and readily reacts with sulphuretted hydrogen, forming an *oxy-sulphide*, $Os_2O_2S_2,H_2O$. It dissolves in nitric acid to form the tetroxide, and in hydrochloric and hydrobromic acids to form mixtures of salts.

Potassium Osmate, $K_2OsO_4,2H_2O$, is obtained by the addition of alcohol or other reducing agents to the solution of the tetroxide in caustic potash. The liquid then becomes of a fine red colour, and when it is sufficiently concentrated the salt separates out as a crystalline powder. When slowly crystallised it forms octahedra which, according to their size, are of a garnet-red or almost black colour. They possess a sweet astringent taste, and do not undergo change on exposure to dry air, but both in solution and in moist air they decompose, especially on addition of an acid, with formation of tetroxide and lower oxides.

The *sodium* salt crystallises less easily, and yields an aqueous solution having a rose-red colour, from which barium chloride precipitates $BaOsO_4$ as an amorphous, green, flocculent pre-

[1] *J. pr. Chem.*, 1863, **90**, 65. [2] *Zeit. anorg. Chem.*, 1893, **3**, 153.

cipitate, which after a while changes to lustrous, black, prismatic crystals.

Osmium Tetroxide or *Perosmic Anhydride* (commonly called osmic acid), OsO_4.—Very finely divided metallic osmium oxidises slowly at the ordinary temperature, and at about 400° takes fire with formation of the above oxide. The denser the metal the higher is the temperature needed for oxidation. Osmium tetroxide may be obtained also by heating the metal in a current of steam, and by dissolving the lower oxides or the metal in nitric acid or aqua regia. These reagents, however, do not attack the metal after it has been strongly ignited. Osmium tetroxide sublimes in transparent, glistening needles which become soft and may be moulded in the hand like wax, and melt at a lower temperature than this substance. They begin to sublime at a very moderate heat, and the fused oxide boils at 100°, yielding a colourless vapour with a specific gravity of 8·89, which is slightly greater than the calculated value. The crystals dissolve readily in water, forming a colourless liquid which does not redden litmus paper, and possesses a caustic and burning taste. It has a most powerful penetrating smell, somewhat analogous to that of chlorine and iodine. A very small quantity of vapour mixed with air attacks the lungs, giving rise to very serious inflammation of the mucous membrane. As an antidote to the effects of the tetroxide Claus recommends the inhalation of sulphuretted hydrogen, which, however, must be cautiously employed. Osmium tetroxide also acts violently on the skin, causing a painful eruption which can be removed by the use of sulphur baths. The vapour also acts, as has been stated, most violently on the eyes, and may produce most serious consequences.[1]

When heated on red-hot charcoal it deflagrates like nitre. It is easily converted into lower oxides by reducing substances, and its alkaline solution when boiled with a salt of formic acid yields a blue precipitate. Sulphur dioxide colours the aqueous solution yellow, then brown, green, and at last indigo-blue.

It is used in microscopic work for staining preparations, the oxide being reduced to metallic osmium.

[1] Deville and Debray, *Ann. Chim. Phys.*, 1859, [3], **56**, 400 ; *Compt. rend.*, 1874, **78**, 1509.

Osmium and the Halogens.

625 *Osmium Dichloride*, $OsCl_2$, is obtained in very small amount by heating osmium in chlorine, as a brownish-black powder which forms a dark-violet coloured unstable solution in water.

Osmium Trichloride, $OsCl_3$.—When osmic acid is boiled for a long time with concentrated hydrochloric acid and a little alcohol a solution is obtained, which on evaporation yields red crystals of the composition $Os_2Cl_7,7H_2O$, which become olive-green in moist air.[1] This appears to be a mixture of the tri- and tetra-chlorides since, on addition of potassium chloride to the alcoholic solution, potassium osmichloride, K_2OsCl_6, separates, and the filtrate on evaporation yields crystals of the trichloride $OsCl_3,3H_2O$.

Potassium Osmochloride or *Chlorosmite*, $K_3OsCl_6,3H_2O$, is obtained by adding ammonia to a solution of osmium tetroxide in caustic potash, and saturating the liquid, as soon as it has become yellow, with hydrochloric acid. On evaporation, the above salt separates out together with potassium and ammonium chlorides. The latter can be readily separated mechanically. It forms dark-red crystals which effloresce in the air and become pink. It dissolves in water, yielding a cherry-red coloured solution, possessing first a strongly astringent and then a sickly sweetish taste.

Ammonium Osmochloride, $2(NH_4)_3OsCl_6,3H_2O$.—In order to prepare this salt, sulphuretted hydrogen is passed into a hydrochloric acid solution of the tetroxide until it has become red. The liquid is then evaporated with sal-ammoniac, when fine red crystals are deposited resembling the potassium salt.

Osmium Tetrachloride, $OsCl_4$, is obtained by heating the metal in dry chlorine. It forms a red sublimate which dissolves in water, yielding a yellow solution; and this on dilution with more water attains a green tint. On standing, the solution becomes colourless with separation of the lower oxides, whilst hydrochloric acid and osmium tetroxide remain in solution.

Potassium Osmichloride or *Chlorosmate*, K_2OsCl_6, is obtained by gently heating a mixture of the finely divided metal with potassium chloride in a current of chlorine, and also by evaporating the hydrochloric acid solution of the tetroxide with

[1] Moraht and Wischin, *Zeit. anorg. Chem.*, 1893, **3**, 153.

potassium chloride. It crystallises in dark-brown, glistening octahedra, which yield a cinnabar-red powder, and dissolve in water with a yellow colour. Alcohol precipitates the compound from this solution in the form of a red, crystalline powder.

Sodium Osmichloride, $Na_2OsCl_6,2H_2O$, is obtained in a similar way, and crystallises in long, orange-coloured prisms which are easily soluble in water and alcohol.

Ammonium Osmichloride, $(NH_4)_2OsCl_6$, is obtained by the addition of powdered ammonium chloride to a solution of the sodium salt. It is then deposited as a red, crystalline powder, crystallising from dilute solution in brown octahedra.

Another sodium osmium chloride, of the composition Na_6OsCl_{12}, is obtained by the action of hydrochloric acid on sodium sulphonosmate, and crystallises in leaflets.[1] *Potassium osmylchloride*, $K_2(OsO_2)Cl_4$, is formed by treating potassium osmylnitrite with hydrochloric acid; it forms anhydrous, red octahedra, and yields a hydrate with $2H_2O$ which forms pale-brown, triclinic crystals.[2]

Osmium and Bromine.—When osmic acid is boiled with hydrobromic acid and a little alcohol, and the solution evaporated, dark-brown, prismatic crystals of the composition $Os_2Br_9,6H_2O$ are obtained, which are possibly a mixture of $OsBr_3$ and $OsBr_6$. *Osmibromides* have also been prepared.

Osmium and Iodine.—By the action of boiling hydriodic acid on osmic acid, violet-black crystals are formed having a metallic lustre, the composition of which appears to be OsI_4 (Moraht and Wischin). When a solution of potassium iodide, strongly acidified with hydrochloric or phosphoric acid, is added to one of osmium tetroxide, a green substance of the composition $OsI_2,2HI$ is formed. On addition of ether the latter assumes a green colour even when only traces of osmium are present.[3]

Osmium and Sulphur.

626 Metallic osmium burns when heated in sulphur vapour, and sulphuretted hydrogen throws down a dark yellow sulphide of osmium from the hydrochloric acid solution of the oxide. This is slightly soluble in water, giving rise to a dark yellow solution, and easily dissolves in nitric acid.

[1] Rosenheim and Sasserath, *Zeit. anorg. Chem.*, 1899, **21**, 122.
[2] Wintrebert, *Ann. Chim. Phys.*, 1903, [7], **28**, 15.
[3] Alvarez, *Chem. News*, 1905, **91**, 172.

Osmium Tetrasulphide, OsS_4, is thrown down as a brown precipitate when sulphuretted hydrogen is passed through an aqueous solution of osmium tetroxide. It is insoluble in alkalis and the sulphides of the alkali metals.

Osmium Sulphite, $OsSO_3$.—In order to prepare this salt, sulphur dioxide is led into an aqueous solution of the peroxide, and sodium sulphate added to the blue liquid. The dark blue gelatinous precipitate, after washing, is dried and yields a powder which is unalterable in the air, and which on trituration exhibits a metallic silvery lustre. If the blue solution be treated with caustic potash a blackish-blue precipitate of hydroxide is obtained, which on exposure to air absorbs oxygen as rapidly as ferrous hydroxide.

Osmium forms a large number of complex sulphites, which crystallise well and are stable substances. *Sodium osmisulphite*, $Na_8[Os(SO_3)_6],8H_2O$, is obtained by boiling a solution of sodium osmichloride with concentrated sodium hydrogen sulphite, and crystallises in brownish-white prisms. Crystalline compounds have been obtained in which one or more of the SO_3 groups are replaced by the groups Cl or H_2O.

Complex sulphites of a different series, known as the *sulphonosmates*, are obtained by passing sulphur dioxide through a solution of osmium tetroxide, and then adding an alkali hydrogen sulphite. The *sodium* salt has the composition $3Na_2O,OsO_3,4SO_2,5H_2O$, its constitution being probably $(ONa)_2Os(SO_3Na)_4,5H_2O$. It crystallises in bright brown needles, and is readily soluble in water at 50°, forming a reddish-brown solution, which soon decomposes with precipitation of a black oxide.[1]

Osmium and Nitrogen.

627 Like the other metals of this sub-group, osmium forms complex derivatives with ammonia, but these have not as yet been fully investigated. It also forms complex nitrites, a peculiar acid termed osmiamic acid, $OsNO_3H$, and derivatives containing nitrogen but free from hydrogen and oxygen termed the nitrilo-compounds, which are obtained by the action of acids on the osmiamates.[2]

[1] Rosenheim and Sasserath, *Zeit. anorg. Chem.*, 1899, **21**, 122; 1900, **24**, 420.

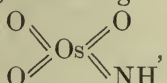
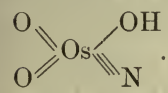
[2] See Werner and Dinklage, *Ber.*, 1906, **39**, 499; Brizard, *Ann. Chim. Phys.*, 1900, [7], **21**, 311.

Osmosammine Hydroxide, $Os[(NH_3)_2(OH)_2]$, is obtained by dissolving the tetroxide in an excess of concentrated ammonia, and heating the reddish-yellow solution in a closed vessel to 50°, when a black precipitate is formed. The flask is then opened and the solution evaporated at a low temperature until the excess of ammonia has been driven off. The base is thus obtained in the form of a blackish-brown powder, which when heated decomposes with rapid evolution of gas. With acids it forms amorphous salts.

Osmyldiammine Chloride, $OsO_2(NH_3)_4Cl_2$, is obtained by the addition of ammonium chloride to a solution of potassium osmate, and forms a yellow, crystalline precipitate easily soluble in water, the solution soon undergoing decomposition.[1]

Osmiamic Acid, $OsNO_3H$.—Osmiamates are formed by the action of ammonia on the tetroxide, especially in the presence of potash, the potassium salt being more stable than the ammonium compound. It was at first supposed[2] that this substance had the formula $K_2N_2Os_2O_5$, but Joly[3] has shown that the true formula is $KNOsO_3$, its formation being represented by the equation:

$$OsO_4 + KOH + NH_3 = KNOsO_3 + 2H_2O.$$

The acid, according to Werner and Dinklage,[4] has the constitution  , being formed from the tetroxide by the replacement of one oxygen atom by the imido-group NH. The salts are probably derived from the tautomeric form  .

The free acid is obtained by decomposing the barium salt with dilute sulphuric acid, or the silver salt with hydrochloric acid. The light-yellow solution remains in the dilute state without change for some time. In the concentrated condition, however, it decomposes with evolution of gas and separation of a brown powder.

Potassium Osmiamate, $KNOsO_3$, forms orange-yellow tetragonal pyramids, which dissolve slowly in cold, and more readily in hot water, and on recrystallisation become dark-coloured, owing to partial decomposition. It decomposes when

[1] See also Wolcott Gibbs, *Amer. J. Sci.*, 1873, **3**, 233.

[2] Fritzsche and Struve, *Petersb. Acad. Bull.*, 1863, **6**, 81.

[3] *Compt. rend.*, 1891, **112**, 1442.

[4] *Ber.*, 1906, **39**, 499.

heated, with loss of nitrogen. Crystalline salts of sodium, barium, and silver are also known.

Osmium Nitrite, $Os(NO_2)_3$, is prepared from barium osminitrite by precipitating the barium exactly with sulphuric acid, and evaporating the resulting solution of osminitrous acid. It forms a deep-brown powder.

The double nitrites with the alkali metals and those of the alkaline earths, and of magnesium and zinc, crystallise well, and are soluble in water.[1] *Sodium osminitrite*, $Na_2Os(NO_2)_5,2H_2O$, crystallises in orange-yellow parallelopipeds, and the remaining osminitrites form similar crystals, the colour of which varies from pale to full orange-yellow. Many other complex nitrites and nitroso-derivatives of osmium have been prepared,[2] some of which contain the osmyl group OsO_2.

Osmium and Carbon.

628 Osmium forms a series of osmocyanides, derived from divalent osmium, which correspond closely in composition and in their properties to the ferrocyanides. The most important of these compounds are the following:

Osmocyanic Acid, $H_4[OsCy_6]$, is deposited in the form of white scales on the addition of fuming hydrochloric acid to a solution of the potassium salt. These are easily soluble in alcohol, and crystallise out from the alcoholic solution on the addition of ether in colourless glistening transparent hexagonal prisms. Its aqueous solution has an acid reaction, and from it a substance of the empirical formula $OsCy_2$ separates out as a dark-violet precipitate, which is, however, probably a complex osmium osmocyanide.

Potassium Osmocyanide, $K_4[OsCy_6],3H_2O$, is obtained by adding potassium cyanide to an alkaline solution of osmium tetroxide, evaporating the filtered solution and heating the residue. It crystallises from hot water, in which it is easily soluble, in yellow tetragonal tablets; these when heated give off water and become colourless. Its solution yields a light-blue precipitate with ferrous salts, which becomes darker-coloured on exposure to air; when treated with nitric acid it is converted into a fine violet-coloured powder, which is also obtained

[1] Wintrebert, *Compt. rend.*, 1905, **140**, 585.
[2] Wintrebert, *Ann. Chim. Phys.*, 1903, [7], **28**, 15.

by precipitating the potassium salt with ferric chloride. After drying this forms a fragile mass having a copper-red colour, and when boiled with caustic potash it yields ferric hydroxide and potassium osmocyanide.

Barium Osmocyanide, $Ba_2[OsCy_6],3H_2O$, is formed when the iron precipitate is boiled with baryta. It crystallises in small yellowish-red transparent rhombic prisms, which are readily soluble in water and alcohol.

Potassium Barium Osmocyanide, $K_2Ba[OsCy_6],3H_2O$, is obtained by mixing hot solutions of the potassium and barium salts. On cooling small yellow oblique rhombohedra are deposited, which are sparingly soluble in cold water.

Detection and Estimation of Osmium.

629 The presence of this metal may be most easily detected by the formation of the volatile strongly-smelling tetroxide. Sulphuretted hydrogen throws down a precipitate of the sulphide insoluble in ammonium sulphide. If a solution contain a mixture of the platinum metals, and other metals precipitable by sulphuretted hydrogen, this gas is passed into the hot solution so long as a precipitate is formed. This is then washed and warmed with yellow ammonium sulphide, when platinum, iridium, gold, &c., dissolve. The filtrate is then acidified with hydrochloric acid, the precipitate fused with sodium carbonate and sodium nitrate, and the fused mass lixiviated with water, the residue being treated according to the method described under platinum (see p. 1404). In this way the iridium is obtained together with platinum and gold, and these may be readily separated. The portion insoluble in ammonium sulphide is then fused with caustic potash and potassium chlorate, and treated with water in order to dissolve the potassium salts of ruthenic and osmic acids. The solution is carefully neutralised with nitric acid in order to separate the black oxide of ruthenium, and the filtrate distilled with nitric acid, when the volatile osmium tetroxide passes over. The residue insoluble in water is gently ignited in a current of hydrogen, and treated with dilute nitric acid, when palladium and rhodium remain behind, and these are separated by aqua regia, in which the latter metal is insoluble.

Osmium is usually estimated *quantitatively* as the metal. It is separated from other metals as the volatile tetroxide, the vapours of which, in order to avoid loss, are passed into caustic potash; alcohol is added to the distillate in order to form potassium osmate, and the solution then treated with ammonium chloride and the precipitated osmyldiammine chloride ignited in hydrogen, when the metal is obtained.

Osmium tetroxide may also be estimated by adding dilute sulphuric acid and potassium iodide to its aqueous solution, and titrating the liberated iodine with sodium thiosulphate. One molecule of osmium tetroxide liberates four atoms of iodine.[1]

The Atomic Weight of osmium was determined by Berzelius in 1828 in a similar way to that of platinum, and he obtained the number 198·9, whilst Frémy,[2] in 1844, by converting the metal into the tetroxide obtained the number 199·6. According to these determinations the atomic weight of osmium appeared to be greater than that of iridium, whereas the analogies of the metal with ruthenium seemed to indicate that it should precede iridium in the periodic system, just as ruthenium precedes rhodium. In 1888 Seubert[3] redetermined the atomic weight by analysing pure potassium and ammonium osmichlorides and obtained the number 191·4, whilst in 1891 from a later[4] and more concordant series of experiments he obtained the still lower number 190·6. The value now (1913) adopted is 190·9.

IRIDIUM. Ir = 193·1.

630 The history of the discovery of this metal has already been described under osmium.

Iridium is found in the platinum ores in considerable quantity in the form of the alloys platiniridium and osmiridium. The first of these occurs in grains, and often in small cubes with rounded edges; the second usually in flat, irregular grains, and occasionally in hexagonal prisms. The composition of these minerals is shown in the following analyses:

[1] Klobbie, *Journ. Chem. Soc.*, 1899, **76**, ii, 184.
[2] *Ann. Chim. Phys.*, 1844, [3], **12**, 514.
[3] *Ber.*, 1888, **21**, 1839.
[4] *Annalen*, 1891, **261**, 257.

	Platiniridium.		Osmiridium.			
	Urals.	Brazil.	Urals.	New Granada.	California.	Australia.
Iridium . .	76·85	27·79	55·24	57·80	53·50	58·13
Osmium . .	—	—	27·23	35·10	43·40	33·46
Platinum .	19·64	55·44	10·08	—	—	—
Rhodium .	—	6·86	1·51	0·63	2·60	3·04
Ruthenium .	—	—	5·85	6·37	0·50	5·22
Palladium .	0·89	0·49	trace	—	—	—
Iron . . .	—	4·14	trace	0·10	—	—
Copper . .	1·78	3·10	trace	0·06	—	0·15
	99·16	97·82	99·91	100·06	100·00	100·00

Iridium is usually prepared from the alloys described above which are left behind when platinum ores are treated with aqua regia. One of the most efficacious of the many methods[1] which have been proposed for the extraction of the metal is that employed by Deville and Debray[2] in the production of the pure iridium required for the standard metre bars of platinum-iridium prepared for the International Commission on the Metric System. The osmiridium is fused with zinc, and heated until all the zinc evaporates, the porous residue being then powdered and ignited with barium nitrate, which converts the iridium into oxide and the osmium into barium osmate. The residue after extraction with water is boiled with nitric acid, which brings the iridium into solution, whilst the osmium is volatilised in the form of tetroxide. The iridium oxide is precipitated from the residual solution by baryta, dissolved in aqua regia, and then thrown down as the double chloride of iridium and ammonium. This, on ignition, yields spongy iridium, containing small quantities of platinum, ruthenium, and a little rhodium. The metal is then ignited with potassium nitrate, and the mass treated with water, when potassium ruthenate dissolves. It is lastly fused with lead, the regulus

[1] Wöhler, *Pogg. Ann.*, 1833, **31**, 161; Claus, *Annalen*, 1858, **107**, 134; Gibbs, *Amer. J. Sci.*, 1861, [2], **31**, 70; Matthey, *Proc. Roy. Soc.*, 1879, **28**, 463.

[2] *Compt. rend.*, 1874, **78**, 1502.

obtained leaving, after treatment with nitric acid and aqua regia, a residue of pure iridium.

Another method frequently employed is to mix the "osrid" with sodium chloride and heat to redness in an atmosphere of chlorine. The metals are then converted into chlorides, and the osmium chloride, being volatile, is expelled. The mixed chlorides are then dissolved in water and the solution is treated with chlorine and hydrochloric acid and excess of potassium chloride added. A precipitate of the double chlorides of potassium and platinum, iridium, and ruthenium is produced, which is filtered off and boiled with water. A current of hydrogen is then passed through the solution when platinum and ruthenium are precipitated and the solution becomes green in colour. The solution is decanted from the precipitated metals and hydrogen again passed through, when the iridium slowly separates out as bright lustrous, thin laminæ.

After osmium, iridium is the most difficultly fusible and least volatile of the platinum metals, but it may be fused and volatilised in the electric furnace; the melting point is 2300°. The molten metal dissolves carbon, which separates out on cooling as graphite. It possesses a white lustre, resembling that of polished steel. In the cold it is very brittle, but at a white heat it is somewhat malleable. The specific gravity of the fused metal is 21·15, whilst that of the crystallised metal is 22·4. If the alcoholic solution of the sulphate be exposed to sunlight the metal is deposited as an extremely fine impalpable black powder, which, when washed with hot water and dried, acts even more energetically in bringing about the combination of combustible gases than does platinum black. The smallest trace brought on to paper saturated with alcohol produces ignition, the metal at the same time being converted into a grey sponge. Spongy iridium is prepared by igniting the double chloride of iridium and ammonium. This oxidises when heated in the air, and when ignited becomes dense and lustrous, and then absorbs oxygen only slowly, whilst the coherent metal does not do so at all. Iridium black, as well as the coherent metal, when alloyed with much platinum, dissolves in aqua regia. Pure massive iridium is, however, not attacked. When it is heated with acid potassium sulphate, or in presence of fused alkalis, it is oxidised, and it unites directly with chlorine at a dull-red heat. When the metal is held in the middle of a flame of alcohol it becomes covered with a black moss-like

deposit, which has the composition IrC_4, and easily takes fire on exposure to the air. The metal is in this case penetrated throughout its mass with carbon, and becomes of a dark-grey colour. The oxides also are converted into the carbide of iridium, with evolution of light and heat, when they are heated in gases or vapours containing carbon.

Owing to its brittleness it is very difficult to roll it into foil or draw it out into wire. These difficulties, however, have recently been overcome. Sir William Crookes recommends the use of iridium for crucibles, and such crucibles have been made by Messrs. Johnson and Matthey.

Iridium is sometimes used for pointing gold pens, and is first heated with phosphorus, which renders it more fusible and easy to work. The phosphorus is afterwards removed by heating the mass in a lime crucible.

It forms an alloy with 9 parts of platinum, which is extremely hard, as elastic as steel, perfectly unalterable in the air and capable of taking an exceedingly fine polish. This alloy has been employed in the production of standard metre bars and for making electrodes to be used in corrosive liquids. A similar alloy is used for the wires employed in high temperature pyrometers.

Colloidal Iridium is obtained by the reduction of iridium salts with hydrazine hydrate in presence of sodium protalbate or lysalbate [1] or gum arabic.[2]

COMPOUNDS OF IRIDIUM.

631 Iridium forms two basic oxides, the sesquioxide, Ir_2O_3, and the dioxide, IrO_2, and two corresponding series of salts, the sesqui-salts, of the general formula IrR^I_3 and the iridic salts IrR^I_4. The halogen compounds form double salts with the corresponding alkali compounds, which must be looked upon as alkali salts of complex acids. Compounds in which the metal is divalent are also known, but have only been slightly investigated. Like the other members of this group, iridium forms numerous complex derivatives, the chief of which are the halogen derivatives just mentioned, the double cyanides, and the ammoniacal derivatives.

[1] Paal and Amberger, *Ber.*, 1905, **38**, 1398; 1907, **40**, 1392, 2201.
[2] Gutbier and Hofmeier, *J. pr. Chem.*, 1905, [2], **71**, 358.

Iridium and Oxygen.

632 *Iridium Sesquioxide*, Ir_2O_3, is formed when potassium iridichloride, K_2IrCl_6, is mixed with sodium carbonate and heated to dull redness:

$$2K_2IrCl_6 + 4Na_2CO_3 = Ir_2O_3 + 8NaCl + 4KCl + 4CO_2 + O.$$

The fused mass is washed with water containing ammonium chloride, and the residue, after ignition to expel the ammonium chloride, is treated with dilute acid in order to remove the small quantity of alkali. A bluish-black powder is thus obtained which begins to decompose when heated above 800°, and at temperatures somewhat above 1000° is completely resolved into oxygen and the metal.

Deville and Debray[1] have investigated this subject, observing the dissociation into metal and oxygen which the oxide undergoes when heated in a porcelain tube. At a temperature of 1139° the oxide rapidly gives off oxygen, and metallic iridium remains behind in the tube. The dissociation pressure at the several temperatures was found to be as follows:

T°.	Pressure.
823°	5 mm.
1003°	203 „
1112°	711 „
1139°	745 „

Iridium sesquioxide is reduced by hydrogen at the ordinary temperature. In the pure state it imparts to porcelain after firing a fine black colour, and when mixed with zinc oxide it yields a grey tint.

Iridium Trihydroxide, $Ir(OH)_3$, is obtained by a process similar to that employed for the preparation of the corresponding rhodium compound, which it closely resembles. If a small quantity of caustic potash be added to a solution of potassium iridiochloride, and the solution allowed to stand in a closed bottle, a yellowish-green precipitate of the hydroxide falls down, which readily dissolves in alkalis and oxidises quickly in the air.

Iridium Dioxide, IrO_2, is a black powder obtained by heating the hydroxide in a current of carbon dioxide, and is said to be

[1] *Compt. rend.*, 1878, **87**, 441.

formed when the metal is heated to bright redness in the air.[1] It is insoluble in acids.

Iridium Tetrahydroxide, $Ir(OH)_4$, is formed by the oxidation of the trihydroxide in the air, or by precipitating the tetrachloride with an alkali, as well as by boiling potassium iridate with ammonium chloride. It is a heavy indigo-blue powder which is almost insoluble in dilute sulphuric and nitric acids, but dissolves completely, though slowly, in hydrochloric acid. Its solubility, however, appears to depend on the method of preparation.[2] On heating the indigo-blue solution it becomes green and then brown.

Potassium Iridate is obtained as a partially soluble bluish mass when iridium is ignited with potassium nitrate. Its composition is not definitely known.

Salts of Iridium.

633 *Iridious Chloride*, $IrCl_2$, is formed as a green insoluble mass when chlorine is passed over spongy iridium at a red heat, and when the tetrachloride is heated.

Iridium Trichloride, $IrCl_3$, is prepared by heating one of its double salts with sulphuric acid. If the mass be then thrown into water the chloride separates out as a light olive-green precipitate insoluble in acids and in alkalis. It is obtained in solution by treating the hydrochloric acid solution of the tetrahydroxide with sulphur dioxide until it has become green, and may also be prepared by heating ammonium iridichloride in chlorine at 440°.[3] It forms complex derivatives with the chlorides of phosphorus and arsenic.[4]

Potassium Iridiochloride or *Chloriridite*, $K_3IrCl_6,3H_2O$, is best obtained from the corresponding iridichloride by heating it with sulphuretted hydrogen, and adding potassium chloride to the olive-green solution. It forms very soluble, green, rhombic prisms which effloresce readily. The sodium and ammonium salts are similar compounds of the formulæ $Na_3IrCl_6,12H_2O$ and $(NH_4)_3IrCl_6,H_2O$.

Iridium Tetrachloride or *Iridic Chloride*, $IrCl_4$, is obtained by dissolving the finely divided metal in aqua regia, or by the solution of the blue hydroxide in hydrochloric acid. When the

[1] Geisenheimer, *Compt. rend.*, 1890, **110**, 855.
[2] See also Joly and Leidié, *Compt. rend.*, 1895, **120**, 1341.
[3] Antony, *Gazz.*, 1893, **23**, i, 184.
[4] Geisenheimer, *Compt. rend.*, 1890, **110**, 1004, 1336.

solution is evaporated at a temperature not above 40°, a black mass is obtained which appears red in thin films, and contains a small quantity of trichloride. The hydrochloric acid solution probably contains *iridichloric acid*, H_2IrCl_6, corresponding to the following compounds.

Potassium Iridichloride or *Chloriridate*, K_2IrCl_6, is obtained by the addition of potassium chloride to the above hydrochloric acid solution. On evaporation small blackish-red regular octahedra are deposited. These are slightly soluble in cold, and more readily in hot water, but do not dissolve in a saturated solution of an alkali chloride or in alcohol.

Sodium Iridichloride, $Na_2IrCl_6,6H_2O$, is readily soluble in water and crystallises in almost black tablets or prisms, which are isomorphous with the corresponding platinum compound.

Ammonium Iridichloride, $(NH_4)_2IrCl_6$, is obtained by precipitating the acid solution of the chloride by ammonium chloride. It is a dark cherry-red powder, consisting of small blackish-red octahedra. One hundred parts of water dissolve 0·699 part of the salt at 14·4°, and 1·266 parts at 39·4°.[1]

Iridium Tribromide, $IrBr_3,4H_2O$.—When the blue hydroxide is dissolved in hydrobromic acid, a blue liquid is obtained which loses bromine on evaporation and deposits small, light olive-green, six-sided crystals, having the above composition. They dissolve readily in water but are not soluble in alcohol, and lose their water of crystallisation at 100°. From the mother-liquor of this salt steel-grey needles of iridiobromic acid, $H_3IrBr_6,3H_2O$, are deposited, having a metallic lustre by reflected light. These, when heated to 100°, lose water and are converted into a brownish-red mass which is easily soluble in water and alcohol. The solution decomposes carbonates with formation of iridiobromides.

Potassium Iridiobromide, $K_3IrBr_6,3H_2O$, forms long olive-green, lustrous, four-sided needles which effloresce on exposure, becoming light-green and opaque. They dissolve readily in water.

Ammonium Iridiobromide, $2(NH_4)_3IrBr_6,3H_2O$, is obtained by reducing the corresponding iridiobromide with sulphur dioxide and neutralising with ammonium carbonate. It crystallises in dark olive-green prisms, and is isomorphous with the corresponding rhodium salt, with which it crystallises in all proportions.

Iridium Tetrabromide, or *Iridic Bromide*, $IrBr_4$.—The blue

[1] Rimbach and Korten, *Zeit. anorg. Chem.*, 1907, **52**, 406.

hydroxide dissolves in hydrobromic acid, giving rise probably to *iridibromic acid*, H_2IrBr_6. This on evaporation with nitric acid leaves a blue deliquescent crystalline mass. It forms, with other bromides, well crystallised iridibromides, such as K_2IrBr_6, which crystallises in opaque, lustrous, blackish-blue regular octahedra.

Iridium Tetriodide, or *Iridic Iodide*, IrI_4, is obtained by boiling the hydrochloric acid solution of the chloride with potassium iodide. It forms a black powder, which yields, with the iodides of the alkali metals, well crystallised double compounds possessing a ruby-red colour.

Iridium Monosulphide, IrS.—The metal burns when ignited in sulphur vapour, giving rise to this compound, which resembles galena in its appearance.

Iridium Sesquisulphide, Ir_2S_3, is precipitated when sulphuretted hydrogen is passed into a solution of a salt of iridium sesquioxide. It is a brown powder, somewhat soluble in pure water, and slightly so in potassium sulphide, and nitric acid.

Iridium Ammonium Pentadecasulphide, $(NH_4)_3IrS_{15}$, crystallises in large brown tetragonal octahedra.[1]

Iridium Disulphide, IrS_2, is formed when the powdered metal is heated with sulphur and sodium carbonate, and is formed by the action of sulphuretted hydrogen on lithium iridichloride at 4°. It is a brown powder, insoluble in nitric acid, and decomposes at 300° into its elements.[2]

Iridious Sulphite has not itself been prepared, but several double salts with sodium sulphite, such as $IrSO_3,3Na_2SO_3$, $10H_2O$ and $IrH_2(SO_3)_2,3Na_2SO_3,4H_2O$, have been described by Seubert,[3] who obtained them during the separation of iridium from rhodium according to Bunsen's method.

Iridium Sesquisulphite, $Ir_2(SO_3)_3,6H_2O$, is obtained when the hydroxide suspended in water is treated for some time with sulphur dioxide. This compound is found in solution whilst a brown basic salt remains undissolved. The solution is then evaporated, when the normal sulphite separates out in the form of a yellow crystalline precipitate which is scarcely soluble in water but dissolves readily in dilute acids. It also forms a number of double salts.

Iridium Sesquisulphate, $Ir_2(SO_4)_3,xH_2O$, crystallises out when

[1] Hofmann and Höchtlen, *Ber.*, 1904, **37**, 245.
[2] Antony, *Gazz.*, 1893, **23**, i, 184.
[3] *Ber.*, 1878, **11**, 1761

a solution of the trihydroxide in sulphuric acid is evaporated in absence of air. It combines with the sulphates of the alkali metals, ammonium and thallium, forming a series of alums having the general formula $M^{I}_2SO_4,Ir_2(SO_4)_3,24H_2O$, which all crystallise in yellow octahedra.[1]

A double salt of the composition $Ir_2(SO_4)_3,3K_2SO_4,2H_2O$ has also been obtained, which separates from boiling aqueous solution on cooling, in rectangular or hexagonal crystals.[2]

Iridic sulphate, $Ir(SO_4)_2$, was obtained by Berzelius as a yellowish-brown amorphous mass. When warmed with sulphuric acid it undergoes reduction forming a green solution of the sesquisulphate.[3]

Iridionitrites.—The simple nitrite of iridium has not been prepared as it readily forms complex nitrites.

Hydrogen Iridionitrite, $H_3[Ir(NO_2)_6],H_2O$, forms light-yellow, readily soluble needles.[4]

Potassium Iridionitrite, $K_3[Ir(NO_2)_6]$, is best prepared by adding potassium nitrite to a solution of iridium sesquisulphate at 70–80.° It is a white powder, readily soluble in boiling water, but almost insoluble in the cold liquid, and in potassium chloride solution. The corresponding *sodium* salt crystallises with $2H_2O$.[5]

Cyanogen Derivatives of Iridium.—The chief of these are the iridicyanides, which resemble the ferricyanides, and have been investigated by Martius.[6]

Potassium Iridiocyanide, $K_4[Ir^{II}Cy_6]$, is obtained in colourless prisms when potassium ferrocyanide is gently ignited with iridium.

Iridicyanic Acid, $H_3[Ir^{III}Cy_6]$, is obtained by decomposing the barium salt with dilute sulphuric acid. It is very soluble in water and alcohol, less so in ether, and is deposited from solution in crystalline crusts. It possesses an acid reaction and has an unpleasant taste, and from its solutions hydrochloric acid precipitates a green substance which is probably a complex iridium iridicyanide.

Potassium Iridicyanide, $K_3[IrCy_6]$, is obtained by fusing

[1] Marino, *Zeit. anorg. Chem.*, 1904, **42**, 213.

[2] Delépine, *Compt. rend.*, 1906, **142**, 1525.

[3] Rimbach and Korten, *Zeit. anorg. Chem.*, 1907, **52**, 406.

[4] Gibbs, *Ber.*, 1871, **4**, 280.

[5] Leidié, *Bull. Soc. chim.*, 1902, [3], **27**, 936; see also Miolati, *Atti R. Accad. Lincei*, 1902, [5], **11**, ii, 151.

[6] *Annalen*, 1861, **117**, 357.

ammonium iridichloride with potassium cyanide, and also by the decomposition of the barium salt with potassium sulphate. It crystallises in colourless tetragonal prisms, which are easily soluble in water, but insoluble in alcohol. It is a very stable body, which is not attacked when heated in chlorine or in hydrogen chloride.

Barium Iridicyanide, $Ba_3[IrCy_6]_2,18H_2O$.—In order to prepare this compound the crude potassium salt is precipitated with copper sulphate, and the precipitate decomposed with baryta water. It forms hard, transparent, probably tetragonal crystals, which effloresce on exposure, are easily soluble in water, and are attacked with difficulty by acids.

Ammoniacal Derivatives of Iridium.

634 Iridium forms ammoniacal derivatives corresponding to iridious chloride, $IrCl_2$, and iridic chloride, $IrCl_4$, which are analogous to the corresponding platinum compounds (p. 1398). It forms also an extended series[1] of compounds corresponding to the trichloride, $IrCl_3$, which are similar to the cobaltic, chromic, and rhodic compounds, and are most probably strictly analogous to these in constitution.

1. *Iridious Compounds.—Dichloro-diammine-iridium* (*Iridiosammonium Chloride*), $[Cl_2(NH_3)_2Ir]$, is obtained by heating a solution of iridious chloride with an excess of ammonium carbonate and neutralising the solution with dilute hydrochloric acid. It is a yellow granular body, insoluble in water. The corresponding hydroxide is not known, and of the other salts only the *sulphato-compound*, $[SO_4(NH_3)_2Ir]$, has been prepared. This is obtained by heating the chloride with sulphuric acid, when an easily soluble orange-coloured crystalline powder is formed.

Tetrammine-iridium Dichloride (*Iridiodiammonium Chloride*), $[(NH_3)_4Ir]Cl_2$, is obtained by prolonged boiling of the preceding chloride with excess of ammonia. On cooling, a whitish precipitate separates, and this is decomposed by boiling water with evolution of ammonia. The hydroxide has not been prepared. The *sulphate* can be obtained from the chloride, and crystallises in rhombic prisms, which are easily soluble in hot water and deflagrate on heating.

[1] Palmaer, *Ber.*, 1889, **22**, 15; 1890, **23**, 3810; 1891, **24**, 2090; *Zeit. anorg. Chem.*, 1895, **10**, 320; 1896, **13**, 211.

2. *Iridic Compounds.—Dichloro-tetrammine-iridium Dinitrate* (*Irididiammonium Chloronitrate*), $[Cl_2(NH_3)_4Ir](NO_3)_2$, is formed when concentrated nitric acid is gradually added to dichloro-diammine-iridium. It dissolves in hot water, and crystallises in lustrous laminæ. If an excess of hydrochloric acid be added to a solution of this compound, the *chloride* is precipitated, crystallising from boiling water in violet octahedra. Silver nitrate precipitates only the half of the chlorine which it contains. Sulphuric acid converts the nitrate into the corresponding *sulphate*, $[Cl_2(NH_3)_4Ir]SO_4$, which crystallises in fine greenish needles.

3. *Iridium Sesqui-compounds.—Hexammine-iridium trichloride*, $[(NH_3)_6Ir]Cl_3$, is prepared by heating the following compound with ammonia at 140°, and crystallises in colourless prisms.

Chloro-pentammine-iridium dichloride (*Purpureo-iridium chloride*), $[Cl(NH_3)_5Ir]Cl_2$, is produced by the action of ammonia on ammonium iridiochloride, and forms yellowish-brown octahedral crystals, but has also been obtained as a flesh-coloured crystalline powder. Silver nitrate precipitates only two-thirds of its chlorine.

A large number of other pentammine-iridium derivatives have been described, as well as aquo-pentammine, tetrammine, and triammine compounds.

Detection and Estimation of Iridium.

635 Ammonium chloride produces, in a tolerably concentrated solution of iridium, a dark-red crystalline precipitate, and the dark colour sometimes observed in the corresponding platinum precipitate indicates the presence of iridium in this metal. Iridium is also distinguished from platinum by the formation of a colourless solution of potassium iridichloride when caustic potash is added to the chloride of the metal, and on exposure to the air this colourless solution first becomes red-coloured, and afterwards blue. Sulphuretted hydrogen decolorises the solution of an iridic salt with separation of sulphur, whilst the brown sulphide, soluble in ammonium sulphide, is precipitated.

Iridium, like platinum, is always estimated quantitatively as the metal.

The Atomic Weight of iridium was determined by Berzelius

by ignitin potassium iridichloride in hydrogen, the result of a single experiment being 196·5. Seubert,[1] in 1878, working with carefully purified material, obtained the number 193·05 by the analysis of the same salt, whilst the ignition of the ammonium salt gave the higher number 193·39. Joly,[2] in 1890, by the analysis of the potassium and ammonium iridiochlorides, obtained the number 193·18.

The number now (1913) adopted is 193·1.

PLATINUM. Pt = 195·2.

636 This metal appears to have been first observed in the sixteenth century; for Scaliger, who died in 1558, in his work *Exercitationes Exotericæ de Subtilitate*, combated the views of Cardanus that all metals are fusible; for, he adds, in the mines of Mexico and Darian a metallic substance is found "quod nullo igni, nullis Hispanicis artibus, hactenus liquescere potuit." As platinum occurs in the above districts it appears very probable that this was the metal here referred to. Indeed the metal seems to have been used long before this date, for an alloy containing platinum together with gold and iridium has been found composing some of the hieroglyphs on an Egyptian box discovered at Thebes, dating from the seventh century B.C.[3]

It was not, however, until the eighteenth century that platinum attracted general attention, and this time many chemists occupied themselves diligently with the subject. The first of these was Don Antonio de Ulloa, who took part in the French Expedition of 1735 which had for its object the measurement of an arc of the meridian on the equator. In 1748 he published his *Relacion Historica del Viage a la America Meridional*, in which he describes an unworkable metallic mineral which even makes gold ore useless if it occur mixed with it in large quantities. William Brownrigg[4] was the first to describe native platinum as a compact metal. He had obtained it nine years previously from Charles Wood, who had brought some samples of it from Carthagena in Granada to Jamaica, and thence to England. Brownrigg termed it a semi-metal. It was afterwards more

[1] *Ber.*, 1878, **11**, 1770. [2] *Compt. rend.*, 1890, **110**, 1131.

[3] Berthelot, *Compt. rend.*, 1901, **132**, 729; *Ann. Chim. Phys.*, 1901, [7], **23**, 5.

[4] *Phil. Trans.*, 1750, **46**, 584.

exactly examined by Scheffer, who describes it in the Memoirs of the Stockholm Academy in 1752 with the title "On White gold, or the seventh Metal, termed in Spanish 'platina del Pinto,'" that is, small silver of Pinto, *platina* being the diminutive of *plata*, the Spanish for silver. The name of del Pinto was added because it was first found in the auriferous sand of that river. Scheffer describes the insolubility of platinum in nitric acid, and was acquainted with the facts that aqua regia dissolves it and that it is precipitated from the solution by mercury. He also states that it is infusible at the strongest heat of a furnace, but that it can be alloyed with other metals, and that it may be fused by the help of arsenic. He declares the new body to be a true metal, and, on account of its unalterability, believes it to be a noble one, and suggests that it may be used for the specula of telescopes. In 1754 Lewis[1] published a series of researches on platinum, and in 1757 the investigations of Marggraf were communicated to the Berlin Academy. Amongst the most important of his observations was that which has since proved of such service to analytical chemistry, that platinum solution produces with the salts of the alkalis an orange-yellow precipitate, with the exception of that of the mineral alkali soda, with which it produces none. Next came Macquer and Beaumé's researches on platinum, which were published in the Memoirs of the Paris Academy of 1758. The most important new fact observed by these chemists was that platinum can be fused in the focus of a powerful burning-glass. Besides this, the paper in question contains the information that platinum had hitherto been so rare a substance, because the Spanish Government had forbidden its exportation, inasmuch as gold could be alloyed with a considerable quantity of the new metal without its colour being sensibly changed, thus giving rise to the possibility of fraud. Further investigations were made by Cronstedt in 1764, and by Bergman in 1777, the latter chemist explaining the nature of the changes which occur when a platinum solution is treated with the alkalis. Count von Sickingen, at that time the representative of the Palatinate at the Court of Paris, worked diligently on the subject of platinum, and was the first, in 1772, to prepare platinum foil and platinum wire, and to show that this metal when alloyed with silver dissolves in nitric acid. His experiments were communicated to the Academy

[1] *Phil. Trans.*, 1754, **48**, 638.

in 1778, and in 1782 the same researches were described in a pamphlet which appeared in German with the title *Experiments on Platinum*. The whole of the preceding researches, as well as many of those carried on at a later time, were made with South American platinum.

In 1819 grains of a white metal were discovered in the auriferous sands of the Urals, but it was not till 1823 that platinum was detected in this substance. This discovery gave rise to the Scientific Expedition to the Urals undertaken by Humboldt, G. Rose, and Ehrenburg, in 1829.

With the exception of *sperrylite*, $PtAs_2$, found in small quantities in the nickel-copper ores of Ontario,[1] platinum occurs in the native state, but native platinum is very seldom pure, the purest specimens having been found in Brazil together with grains of palladium. The usual platinum "ore," as it is termed, contains all the metals of this group together with iron, copper, titanic iron ore, &c. It is sometimes, though seldom, found crystallised in cubes and octahedra, but more usually occurs in rounded or flattened grains, or sand having a metallic lustre, and occasionally in large rounded nuggets, both forms occurring in river sand or detritus. Some of the more important localities from which platinum is obtained are Choco near Popayan, the gold-washings of the Pinto in the province of Antioquia in Columbia, and Minas Geraes in Brazil. In the Urals, it is found in alluvial deposits at Nischnetagilsk and Goroblagodat. Platinum likewise occurs in the Natoos Mountains in Borneo, and in Haiti, Peru, California, India, and Australia, especially in New South Wales, where it is now being worked. It is also found in small quantities in the sands of various rivers, occurring in the Rhine, and in streams in Wicklow, North Carolina, and Canada East. The largest mass which has yet been obtained is that in the Demidoff Cabinet in St. Petersburg, weighing 7·837 kilos. In the Urals platinum is found together with chrome iron ore in serpentine, whilst in the Brazils it occurs with gold in syenite. Many common minerals, such as dolomite, heavy spar, and fahl ore, contain traces of platinum, and this explains the occurrence of the metal in the sands of so many rivers. It is found in small quantities also in most of the ores of lead and silver, and it is usually contained with palladium in

[1] Walker, *Zeit. Kryst. Min.*, 1896, **25**, 561; *Amer. J. Sci.*, 1896, [4], **1**, 110; Wells and Penfield, *ibid.*, 1902, [4], **13**, 95; Dickson, *ibid.*, 1903, [4], **15**, 137.

small quantities in all silver, while its presence has been observed in meteoric iron.[1] Some of the American copper ores contain platinum, and it is recovered in the electrolytic refining of copper. In the United States mints the gold is refined electrolytically, and sometimes the anode sludge contains small quantities of platinum. Thus, in the San Francisco mint, 112 ounces of platinum and iridium were recovered from the refining of 1,073,000 standard ounces of gold.

The following table contains a series of analyses of various platinum ores by Deville and Debray :[2]

Locality.	Choco (S. America).	California.	Australia.	Urals.
Platinum . . .	86·20	85·50	61·40	76·40
Gold	1·00	0·80	1·20	0·40
Iron	7·80	6·75	4·55	11·70
Iridium	0·85	1·05	1·10	4·30
Rhodium	1·40	1·00	1·85	0·30
Palladium . . .	0·50	0·60	1·80	1·40
Copper	0·60	1·40	1·10	4·10
Osmiridium . . .	0·95	1·10	26·00	0·50
Sand	0·95	2·95	1·20	1·40
	100·25	101·15	100·20	100·50

The body termed osmiridium is an alloy of osmium and iridium which is not attacked by aqua regia, and the sand contains quartz, chrome iron ore, hyacinth, spinel, and titanic iron ore.

637 *The Metallurgy of Platinum.*—The infusibility of platinum, as well as its power of withstanding the action of many of the most powerful reagents, rendered it desirable that this metal should be employed for the manufacture of vessels for chemical use. In 1784 Achard mentioned that the substance obtained by fusing arsenic and platinum together leaves, on ignition, a residue of malleable platinum, and in this way he prepared what was in all probability the first platinum crucible. From the

[1] Davison, *Amer. J. Sci.*, 1899, [4], **7**, 4.

[2] *Ann. Chim. Phys.*, 1859, [3], **56**, 449. See also Martin, 16*th Ann. Rept. U. S. Geol. Survey for* 1894–5, Pt. III., 1895, 628.

year 1787 this method was employed in Paris, where Janetty was celebrated for his platinum work. Platinum vessels were, however, then and for some time afterwards so expensive and difficult to obtain, that in the year 1801 G. Rose and Karsten, for want of a platinum crucible, were unable to examine the statement of Guyton de Morveau and Desormes that potash consists of lime and hydrogen, and soda of magnesia and hydrogen.

In the year 1800 Richard Knight[1] published a method for preparing malleable platinum. This consisted in dissolving the crude platinum, precipitating the solution with ammonium chloride, stamping the dried precipitate of the double chloride of platinum and ammonium into a conical mould made of fire clay, and igniting the whole. In this way platinum is obtained as a coherent metallic mass, which can then be worked up. In 1822 a similar method was described by Barrual; but for many years before this, in fact from 1800 to 1809, a relative of a member of the well-known firm of Messrs. Johnson, Matthey and Co. was employed in working on platinum, and had discovered (whether independently of Knight is uncertain) a method for consolidating the sponge, which was afterwards elaborated by Wollaston and described by him in the Bakerian Lecture[2] for 1828. This, although identical in the main features with Knight's process, is distinguished from it in several important particulars, and is the method by which platinum was manufactured up to the year 1859, when Deville's process came into use.[3] Wollaston in the first place pointed out the necessity of heating the double chloride very gently at a temperature just sufficient to expel the whole of the ammonium chloride and to occasion the particles of platinum to cohere as little as possible, for on this depends the ultimate ductility of the product. The metallic powder thus obtained must be rubbed between the hands of the operator so fine as to pass through a fine lawn sieve. After having been well levigated, the uniform mud or pulp is pressed whilst cold into a brass barrel and strongly compressed by a powerful lever. The cake of platinum can be easily removed, owing to the conical form of the barrel, and is so hard that it can be handled without danger of breaking. It is then placed on a charcoal fire and heated to redness to drive off moisture and to give it a greater

[1] *Tilloch's Phil. Mag.*, 1803, **16**, 1. [2] *Phil. Trans.*, 1829, **119**, 1.
[3] *Ann. Chim. Phys.*, 1859, [3], **56**, 484.

degree of cohesion. After this it is heated in a wind furnace to the most intense heat that can be obtained. After ignition for about twenty minutes, the cake is removed from the furnace and placed upright on an anvil, and struck when hot with a heavy hammer. The ingot of platinum thus obtained may be drawn into wire or submitted to any of the processes of which the most ductile metals are capable.

The easy method thus proposed for working up platinum has had a great influence on the progress of chemistry. The present generation of chemists can scarcely understand the difficulties with which their predecessors had to contend, unable, as they were, to use either platinum crucibles, basins, retorts, or platinum foil or wire. In his *Letters on Chemistry* Liebig says:

"Without platinum it would be impossible, in many cases, to make the analysis of a mineral. The mineral must be dissolved and it must be first rendered soluble, or prepared for solution. Now, vessels of glass, of porcelain, and of all non-metallic substances are destroyed by the means we employ for that purpose. Crucibles of gold and silver would melt at high temperatures. But platinum is cheaper than gold, harder and more durable than silver, infusible at all temperatures of our furnaces, and is left intact by acids and alkali carbonates. Platinum unites all the valuable properties of gold and of porcelain, resisting the action of heat, and of almost all chemical agents. Without platinum the composition of most minerals would have yet remained unknown."

Platinum apparatus is also employed on a large scale and with great advantage in the chemical industries; thus, for example, in the manufacture of sulphuric acid, and in the parting of the noble metals. The first platinum apparatus for concentrating sulphuric acid, weighing 423 ounces, was made in London in 1809 by Messrs. Johnson, Matthey and Co., who since that time have furnished platinum vessels for all parts of the world. It is interesting to notice that the price charged for this first platinum still was at the rate of 16*s.* per ounce, the present price (1913) being about £10.

The application of the oxy-hydrogen blowpipe for fusing large masses of platinum, proposed first by Hare,[1] has exerted a great influence on the progress of the platinum industry. Hare succeeded in fusing 971 grams of platinum, as well as large

[1] *Phil. Mag.*, 1847, [3], **31**, 356.

quantities of iridium and osmium. This method was improved upon by Deville and Debray,[1] whose investigations on the platinum metals have been of great service to the general progress of chemical industry. The means employed by these chemists for fusing platinum, and now employed on the large scale by most of the platinum manufacturers, consists in the use of two well-fitting lumps of quick lime. The upper one has a hole drilled through the middle for the introduction of the blowpipe, whilst a side opening permits the escape of the products of combustion and serves as an outlet for the molten metal. Instead of hydrogen, common coal-gas is usually employed. This is allowed to enter through the tube H, Fig. 200, whilst the oxygen enters at O. The upper portion of the blowpipe consists of copper and the lower of platinum. Lime is used for the crucible, because it stands a high temperature well, and at the same time it absorbs the slags of the oxides of iron and silicon and other materials which are formed during the operation. The introduction of this process induced chemists to seek for a cheap method of preparing oxygen on the large scale, whilst by means of the oxy-hydrogen blowpipe Messrs. Johnson, Matthey and Co. have succeeded in effecting a most important improvement in the metallurgy of platinum, viz., that of soldering platinum by itself (autogenous soldering), instead, as was formerly the case, of soldering with gold.

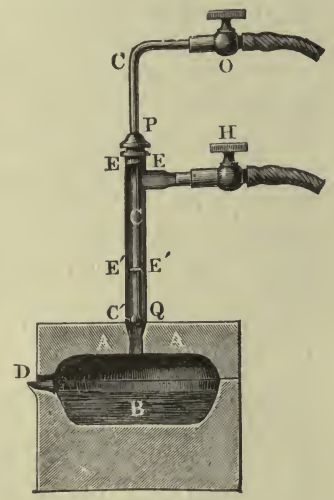


Fig. 200.

The electric furnace is now frequently employed for fusing platinum.

Most of the platinum of commerce is obtained from the Urals in Russia, by a process of concentration by washing, similar to the manner in which alluvial gold is extracted. The crude platinum thus obtained is in the form of fine particles, grains, and scales; nuggets are also occasionally met with, and a little gold is also generally present. This gold is extracted from the

[1] *Ann. Chim. Phys.*, 1859, [3], **56**, 385.

crude platinum by amalgamation, the material being rubbed with mercury in a dish made of wood, iron, or porcelain. The crude platinum which remains may be treated by a dry or a wet method.

Deville and Debray elaborated two methods[1] for treating this crude platinum in the dry way. According to the first of these, the ore is repeatedly melted in a vessel made of lime. In this way an alloy of platinum with iridium and rhodium is obtained. This method is especially applicable to the fusion of old platinum vessels, inasmuch as all the impurities, such as sulphur, phosphorus, iron, gold, lead, &c., which occur in the scrap platinum, are either volatilised or absorbed by the lime. The second method depends on the fact that lead can be alloyed with the platinum metals but not with osmiridium. These processes have, however, not met with much success in practice, inasmuch as there is no guarantee that the platinum thus prepared does not contain, in addition to the iridium and rhodium, which are harmless constituents, other admixtures, or that the metal thus obtained is homogeneous.

Hence, up to the present time, wet methods are more generally used. The following process is adopted in the German works of Heräus in Hanau.[2] The raw ore is treated in glass retorts under a pressure of twelve inches of water with a mixture of 1 part of aqua regia and 2 parts of water. The solution is evaporated to dryness, and the dried mass heated to 125°, at which temperature the palladium and rhodium salts are reduced to lower chlorides. The clear aqueous extract acidified by hydrochloric acid is then precipitated with ammonium chloride, the pure double chloride of platinum and ammonium being thrown down, whilst the corresponding iridium salt is obtained on evaporating the mother-liquor. The solution remaining after precipitating the platinum salt is treated with scrap iron, when the other metals are thrown down, and the precipitate, from which the excess of iron has been dissolved by hydrochloric acid, is again treated with aqua regia, and from this solution a new portion of platinum and iridium thrown down. The mother-liquors, as well as the residue left on dissolving the ore in aqua regia, contain the metals palladium, rhodium, ruthenium, osmium, and iridium. The spongy platinum obtained by igniting the double chloride of platinum and

[1] *Ann. Chim. Phys.*, 1859, [3], **56**, 385; 1861, **61**, 5.
[2] Philipp, *Ber. Entw. Chem. Ind.*, **1**, 999.

ammonium is then pressed, broken up in pieces, and fused with an excess of oxygen in a lime crucible.

In the wet process of G. Matthey the platinum is first melted with six times its weight of lead, and then granulated by pouring into water.

The process employed in Russia is very similar to the foregoing. The crude platinum is dissolved in aqua regia in porcelain basins set on a sand-bath. The solution is repeatedly evaporated with hydrochloric acid until all nitric acid has been removed, the aqueous solution then filtered, and the filtrate treated as described above.[1]

Most of the platinum which occurs in commerce is not pure, but contains, like Russian platinum coin, 2 per cent. of iridium. This alloy is especially valuable for the preparation of chemical vessels, inasmuch as it is less readily attacked by acids than pure platinum.

638 *Preparation of Pure Platinum.*—In order to prepare pure platinum various methods have been proposed. Deville and Debray[2] have prepared it on a large scale by the following process. The metal, which contains iridium and rhodium, is fused with from six to ten times its weight of lead, the mass after cooling treated with nitric acid, and the residue treated with dilute aqua regia, when a crystalline alloy of iridium, ruthenium, and iron remains behind, whilst lead, platinum, and some rhodium go into solution. This latter is treated with ammonium chloride, the double chloride, $(NH_4)_2PtCl_6$, being thrown down in a finely divided, amorphous state and almost white, whilst the rhodium is kept in solution. The precipitate is washed with water containing hydrochloric acid, ignited, and the residue of platinum fused in a lime crucible. When fused the supply of gas is suddenly stopped, so that the metal solidifies from the outside inwards, and in this way the formation of bubbles in the metal is avoided.

According to G. Matthey,[3] the preparation of pure platinum is a matter of great difficulty. His process is, to begin with, similar to that already described, but he evaporates down the aqua regia solution, and then adds pure sulphuric acid to the residue in order to convert any lead which may remain in solution into the insoluble sulphate. The platinichloric acid is then dissolved out with water and precipitated by a mixture of

[1] *Mineral Industry*, 1897, **6**, 551.
[2] *Compt. rend.*, 1875, **81**, 893.
[3] *Proc. Roy. Soc.*, 1879, **28**, 463.

ammonium chloride and common salt, the latter being added because the ammonium platinichloride is less soluble in a solution of common salt than in water. The liquid is then heated to 80° and allowed to stand for some days in order that the precipitate may become denser. This is then repeatedly washed with a solution of ammonium chloride, and at last with distilled water acidified with hydrochloric acid. The washed precipitate is then dried and mixed with potassium bisulphate, to which a small quantity of ammonium bisulphate has been added. The mixture is then heated to dark redness in a platinum basin. On boiling the mass with water, potassium sulphate and potassium rhodosulphate dissolve, leaving pure platinum behind.

The production of platinum from the Ural mines, which are now almost the only source of the metal, has been subject to great variations. In 1825, when the mines were first opened, only 361 pounds were produced. In 1827 the experiment of coining with platinum was tried at the St. Petersburg mint, pieces of 3, 6, and 12 roubles being produced. The coinage of platinum was, however, soon abandoned (in 1844), and the coins in circulation were withdrawn, owing to the very considerable variations which the price of the metal underwent from year to year and the impossibility therefore of fixing a permanent monetary value upon the coin. The total value coined amounted to 4,146,504 roubles, and the annual amount produced towards the close of the period in which the metal was coined reached 7,716·4 pounds. It afterwards declined, but subsequently increased owing to the large demand for the metal occasioned by the widespread introduction of electric lighting, the metal being employed in the construction of incandescent lamps. In 1893 the production reached the amount of 11,196 pounds.

During recent years the supply of platinum has not been equal to the increase in demand; Russia is still the chief source of the metal, and the scarcity is partly due to the local difficulty of securing the necessary mining labour, and also to the diminution of yield in the richer mines. The average output of the Russian mines was, for the years 1893 to 1898, 12,050 lbs. per annum; for the years 1899 to 1904, 12,600 lbs., whilst during the year 1905, 14,050 lbs. were produced. There is, however, a small production of platinum in the United States, between 100 and 200 troy ounces being produced per annum; Columbia also produced 800 lbs. during 1904.

Platinum is largely used for the construction of chemical apparatus employed both in the laboratory and the works, for protecting other metals (platinising), and, in the form of its salts, for the preparation of photographic prints.

The following are the official statistics for the years 1902 to 1911:—

1902	5·98 tons
1903	5·86 „
1904	4·89 „
1905	5·12 „
1906	5·64 „
1907	5·26 „
1908	4·77 „
1909	4·99 „
1910	5·35 „
1911	5·36 „

These figures, however, show only the platinum officially registered. There is a considerable amount of illicit dealing which is variously estimated at 1·6 to 2·4 tons per annum. The Russian output is about 95 per cent. of the world's production, and probably varies between 6·4 and 7·2 tons.

639 *Properties.*—Pure platinum has a tin-white colour, is soft like copper, has a specific gravity of 21·4136–21·4317 (Kahlbaum),[1] and is the most malleable of metals after gold and silver. Like iron, it can be readily welded at a white heat. It melts at 1710° as determined by a resistance thermometer,[2] whereas higher temperatures, 1753–1889°, are indicated by the optical pyrometer method.[3] An extremely fine wire can be melted in the flame of a Bunsen burner; platinum in large masses is infusible even at the highest temperature of a blast-furnace, although a small piece of the metal may be melted in such a furnace.[4] It can, however, be fused in the oxy-hydrogen flame. When large masses of the molten metal are quickly cooled they exhibit the phenomenon of "spitting" so characteristic of silver.

Platinum is stated to volatilise below its melting point, and

[1] *J. Chim. phys.*, 1904, **2**, 537.

[2] Harker, *Proc. Roy. Soc.*, 1906, **76**, A, 235.

[3] Waidner and Burgess, *Bull. U. S. Bureau Standards*, 1907, **3**, 163; Holborn and Valentiner, *Ann. Physik*, 1907, **22**, 1.

[4] Meyer, *Ber.*, 1896, **29**, 850.

cubic or octahedral crystals of the metal have been found in the neighbourhood of the platinum electrodes in electric furnaces.[1] According to Hulett and Berger[2] it begins to volatilise at 800° in air, whilst it is unchanged at this temperature in the absence of oxygen; this phenomenon has been attributed to the formation at high temperatures of a volatile oxide which undergoes decomposition at lower temperatures. It can be distilled in the electric furnace.[3]

Tubes made from fused and hammered platinum allow hydrogen to pass through them at a strong red-heat in larger quantity than is the case with caoutchouc membranes at the ordinary temperature. This property depends upon the fact that the red-hot metal has the power of absorbing hydrogen (Vol. I., p. 159), taking up 3·8 volumes of the gas, which it gives off on heating in a vacuum, the surface of the platinum becoming in this case covered with bubbles.[4] The same phenomenon is noticed when platinum foil is employed as the negative pole in the electrolysis of water, the absorbed hydrogen being again given off when it is converted into the positive pole.

In January, 1817, Sir Humphry Davy communicated the fact to the Royal Society that mixtures of oxygen or air with hydrogen, carbon monoxide, ethylene, vapour of alcohol, vapour of ether, and other easily inflammable gases or vapours, are capable of bringing about the incandescence of a warmed platinum wire,[5] and that then these mixtures either combine slowly or in some cases quickly, and even with explosion. This now well-known phenomenon is thus described by Davy: "A temperature much below ignition only was necessary for producing the curious phenomenon, and the wire was repeatedly taken out and cooled in the atmosphere till it ceased to be visibly red, and yet when admitted again it instantly became red hot." In the following year Erman observed that it was only necessary to warm the platinum wire to 50° to enable it to bring about this combination.

In 1820 Edmund Davy showed that the black powder deposited when a platinum solution is precipitated by sulphur-

[1] Guntz and Bassett, *Bull. Soc. chim.*, 1905, [3], **33**, 1306.

[2] *J. Amer. Chem. Soc.*, 1904, **26**, 1512.

[3] Moissan, *Compt. rend.*, 1906, **142**, 189.

[4] See also Winkelmann, *Ann. Physik*, 1901, [4], **6**, 104; 1902, [4], **8**, 388; 1906, [4], **19**, 1045.

[5] *Phil. Trans.*, 1817, **107**, 77.

etted hydrogen, the precipitate dissolved in nitric acid, and the liquid thus obtained mixed with its own volume of alcohol, possesses the property, when moistened with spirits of wine, of becoming ignited in the air. Two years later, Döbereiner observed that spongy platinum, obtained by the ignition of the double chloride of platinum and ammonium, exhibits the same phenomenon when gently warmed with alcohol. In 1823 the same chemist noticed that when hydrogen is allowed to pass over spongy platinum in presence of air the hydrogen gas is ignited, and upon this was founded the well-known Döbereiner's Hydrogen Lamp.[1] Faraday afterwards showed that chemically clean platinum acts in a similar way. The circumstances under which platinum and certain other metals exhibit this action

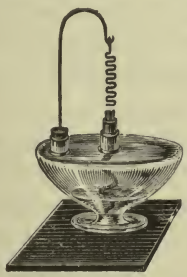


Fig. 201.

Fig. 202.

were investigated by Thénard and Dulong in a research published in the same year.

In order to exhibit this action Davy's glow-lamp is used (Fig. 201). It is fed with a mixture of alcohol and ether, or with methyl alcohol; this is ignited in order to heat the spiral of platinum wire to redness. The flame is then blown out, and the mixed vapours of alcohol and ether rising from the moist wick are oxidised, and thus the spiral is kept brightly incandescent. The same phenomenon can be observed if a spiral of platinum wire be hung in a small test-glass (Fig. 202) into which a little ether has been poured. Another mode of showing the same experiment is to heat a small piece of platinum foil in the flame of a Bunsen burner, and then quickly to extinguish the flame, allowing the gas to escape. The foil soon begins to glow, and if it be placed near the burner it becomes hot enough to re-ignite the gas; if further removed, the foil continues to glow, but the gas is not ignited.

[1] *Schweigger's J.*, **42**, 60; *Tilloch's Phil. Mag.*, 1825, **65**, 150.

Spongy Platinum, first prepared by E. Davy, is very finely divided metallic platinum, which possesses a very large surface compared with its mass, and is able to condense large quantities of oxygen. This substance is frequently employed as an oxidising agent, and may be readily prepared by gently heating the double chloride of platinum and ammonium. It then forms a porous mass, which, when heated strongly, becomes denser, and assumes a metallic lustre under the burnisher.

Platinum Black.—This form of platinum was also discovered by E. Davy, who, however, misled by certain accidental impurities, considered it to be a platinous nitrite. It is to Liebig[1] that we owe the discovery of this error, and also a description of a good method for the preparation of the substance. This consists in warming a solution of platinum dichloride in potash with alcohol. Thus obtained it is a soft black dull powder, which soils any surface on which it is rubbed. When thoroughly freed from alcohol by boiling with water, and dried in a vacuum over sulphuric acid, it absorbs oxygen from the air so rapidly that the mass becomes red-hot. Platinum black is obtained also by dissolving alloys of platinum with other metals, such as copper and zinc, in nitric acid, when the platinum remains in the form of a black powder. This latter preparation, heated in open vessels to a temperature considerably below redness, deflagrates with a hissing noise, sometimes detonating like gunpowder. Platinum black is obtained also when platinum is precipitated by other metals from a dilute solution, or when such a solution is treated with reducing agents. Thus, for instance, if a solution of platinic chloride be allowed to drop into a boiling mixture of three volumes of glycerol and two of caustic potash of specific gravity 1·08, the black obtained possesses extremely active properties,[2] as does that prepared by the reduction of platinic chloride by means of formaldehyde.[3] According to Liebig, platinum black absorbs more than 800 times its volume of oxygen, whereas the black prepared by Mond, Ramsay, and Shields was found to contain 100 volumes of oxygen. When brought into hydrogen 310 volumes were taken up, 200 of which united with the oxygen present to form water, whilst the remaining 110 were absorbed.[4] A certain amount of occluded oxygen can, however, coexist with occluded

[1] *Pogg. Ann.*, 1829, **17**, 102.
[2] Zdrawkowitch, *Bull. Soc. chim.*, 1876, [2], **25**, 198.
[3] Loew, *Ber.*, 1890, **23**, 289. [4] *Proc. Roy. Soc.*, 1895, **58**, 242.

hydrogen in platinum black. It appears probable that platinous hydroxide is formed by the absorption of oxygen, since the heat of occlusion of oxygen by the black is almost identical with the heat of formation of platinous hydroxide.[1] Platinum black after absorbing oxygen dissolves partially in hydrochloric acid as platinous chloride, and the difference between the loss of weight of the black and the amount of platinum in solution also corresponds to the formation of this hydroxide.[2] Moreover, the black containing oxygen is able to bring about oxidising actions similar to those produced by platinous oxide, such as the liberation of iodine from potassium iodide, and the oxidation of arsenious to arsenic acid.[3] After frequent ignition in a mixture of combustible gas and air, the black becomes denser, approaching spongy platinum in its properties. Platinum black is frequently used in organic chemistry as an oxidising agent, and it has been successfully applied in place of oxide of copper in organic analysis.[4] Platinum black also absorbs 60 volumes of carbon monoxide.[5]

Colloidal Platinum may be obtained as a dark-brown solution by passing an electric arc between platinum wires immersed in water. The solution rapidly decomposes hydrogen peroxide,[6] and is capable of causing the union of hydrogen and oxygen.[7] It may also be prepared by means of sodium lysalbate in a similar manner to colloidal gold and silver, and on evaporating the solution and drying at 100° black glistening scales of colloidal platinum are obtained which are soluble in water.[8] Similar solutions are obtained by reducing solutions of platinum salts with other organic reducing agents.[9]

Platinum is scarcely oxidised at any temperature by oxygen, water, or nitric acid. If very thin platinum foil be heated in

[1] Mond, Ramsay, and Shields, *Proc. Roy. Soc.*, 1897, **62**, 50.

[2] Engler and Wöhler, *Zeit. anorg. Chem.*, 1901, **29**, 1 ; Wöhler, *Ber.*, 1903, **36**, 3475.

[3] See also Raschig, *Zeit. angew. Chem.*, 1906, **19**, 1748, 2083 ; Bredig, *ibid.*, 1985 ; Luther, *ibid.*, 2049.

[4] Kopfer, *Journ. Chem. Soc.*, 1877, i, 228 ; Dennstedt, *Ber.*, 1906, **39**, 1623.

[5] Hemptinne, *Zeit. physikal. Chem.*, 1898, **27**, 429.

[6] Bredig, *Zeit. angew. Chem.*, 1898, 951 ; *Zeit. physikal. Chem.*, 1901, **38**, 122 ; Bredig and von Berneck, *ibid.*, 1899, **31**, 353 ; Bredig and Ikeda, *ibid.*, 1901, **37**, 1 ; Raudnitz, *ibid.*, 551.

[7] Ernst, *Zeit. physikal. Chem.*, 1901, **37**, 448.

[8] Paal and Amberger, *Ber.*, 1904, **37**, 124.

[9] Gutbier, *Zeit. anorg. Chem.*, 1902, **32**, 347 ; *J. pr. Chem.*, 1905, [2], **71**, 358 ; Henrich *Ber.*, 1903, **36**, 309 ; Garbowski, *ibid.*, 1215.

oxygen for some weeks at 420–450° it becomes covered with a small quantity of platinous oxide, whilst platinum sponge is more quickly converted into this oxide in the same manner.[1]

It is appreciably attacked by sulphuric acid [2] at 250°, although very slightly so below 200°, and dissolves to a small extent when used for the electrodes in the electrolysis of sulphuric acid, especially when alternating currents are employed.[3] It is not attacked by sulphur alone, although action takes place if alkalis are present. These latter, as well as nitre, oxidise the metal, and for this reason fusion with alkalis or nitre ought not to be performed in platinum vessels. It dissolves in potassium cyanide solution in the absence of oxygen with evolution of hydrogen, the amount dissolved being very small in the cold but increasing on heating.[4] Alkali cyanides should not be fused in contact with platinum, as these likewise attack the metal. It is also inadvisable to expose platinum vessels to direct contact with burning charcoal, as the silicon reduced from the charcoal-ash unites with the metal, making it brittle and liable to crack. Especially to be avoided is contact at a high temperature with compounds of the easily reducible metals, as these readily form fusible alloys with the platinum. Phosphorus and arsenic also combine with heated platinum. When platinum vessels are heated over a smoky flame, or in one in which the supply of air is insufficient to bring about complete combustion, such as the internal zone of a Bunsen burner, the surface of the platinum becomes disintegrated, probably owing to the successive formation and decomposition of compounds of the metal with carbon from the flame.

The best method of cleaning a platinum crucible is to fuse in it some potassium bisulphate (Gmelin), and in order to test whether a new platinum crucible be of proper quality it is first boiled with hydrochloric acid and afterwards with pure nitric acid. If none of the metal be dissolved the platinum is good. The surface of a platinum crucible is best cleaned by being rubbed with moist animal charcoal.

[1] Wöhler, *Ber.*, 1903, **36**, 3475.

[2] Conroy, *J. Soc. Chem. Ind.*, 1903, **22**, 465.

[3] Margueles, *Ann. Phys. Chem.*, 1898, [2], **65**, 629; **66**, 540; Ruer, *Zeit. Elektrochem.*, 1903, **9**, 235; 1905, **11**, 10; Brochet and Petit, *Compt. rend.*, 1905, **140**, 655; *Zeit. Elektrochem.*, 1905, **11**, 441; Senter, *Trans. Faraday Soc.*, 1907, **2**, 1.

[4] Glaser, *Zeit. Elektrochem.*, 1903, **9**, 11; Wöhler, *Ber.*, 1903, **36**, 3475.

COMPOUNDS OF PLATINUM.

Platinum and Oxygen.

640 Three oxides of this metal are definitely known, platinum monoxide or platinous oxide, PtO, giving rise to the platinous salts, platinum dioxide or platinic oxide, PtO_2, giving rise to the platinic salts, and the trioxide, PtO_3. In addition, a sesquioxide, Pt_2O_3, and an oxide, Pt_3O_4, have been described, but doubt has been thrown on their existence.

Platinum Monoxide, PtO, is obtained as a grey powder by the careful ignition of the hydroxide, or as a violet powder by igniting the compound of platinic oxide and lime (see p. 1388), and treating the residue with nitric acid. It is also probably formed to some extent as already mentioned when platinum is heated for some time in oxygen (Wöhler). When strongly heated it passes into the metal, deflagrating when heated with charcoal. It is reduced to platinum black when heated with aqueous formic acid, CH_2O_2, with violent evolution of carbon dioxide.

Platinous Hydroxide, $Pt(OH)_2$, is obtained by decomposing the dichloride with hot caustic potash. The whole of the chlorine cannot, however, be removed in this way, and if caustic soda be employed, a product is obtained from which the soda cannot be completely washed out (Liebig). It is prepared in the pure state by mixing one part of potassium platinochloride, K_2PtCl_4, with twelve parts of water, adding the exact quantity of dilute caustic soda necessary for decomposition and heating the mixture to boiling until the alkaline solution has become neutral. The hydroxide retains its water in a remarkable manner, one sample still containing 6·6 per cent. of water after heating for several days at 405° (Wöhler).[1] It dissolves in hydrochloric, hydrobromic, and sulphurous acids, but not in other oxy-acids. Boiling caustic potash decomposes it into metal and the dioxide. It is an oxidising agent and acts as a weak base, of which the halogen salts, as well as a few double salts of the oxy-acids, have been prepared.

Platinum Dioxide, PtO_2, is obtained as a black powder by gently heating the corresponding hydroxide.

Platinum Hydroxide or *Platinic Hydroxide* is prepared by boiling a solution of platinic chloride with caustic potash, when

[1] *Zeit. anorg. Chem.*, 1904, **40**, 423.

a basic double salt is precipitated, and this is treated with acetic acid in order to dissolve out the alkali. In this way it is obtained as an almost white precipitate, which on drying becomes yellow. This is termed *platinic acid* and probably has the composition [1] $H_2Pt(OH)_6 = PtO_2,4H_2O$, analogous to platinichloric acid, H_2PtCl_6. Platinic hydroxide acts both as a weak base and as an acid-forming oxide. It dissolves in alkalis and the solutions deposit crystalline *platinates* such as $K_2Pt(OH)_6$ isomorphous with the stannates [2]; they do not lose water at 100–110°, and their solutions give with silver acetate a precipitate of $Ag_2Pt(OH)_6$. A reddish-yellow, partially crystalline powder of the composition $Na_2O,3PtO_2,6H_2O$ is obtained when a clear aqueous mixture of platinichloric acid and sodium carbonate is exposed to sunshine, or when the mixture is heated for some time at 100°. The aqueous solution of the two salts may also be evaporated to dryness, and the residue boiled out with water, when a denser precipitate of the same compound is obtained having an ochre-yellow colour. A compound of the composition $Na_2O,5PtO_2,9H_2O$ has also been obtained (Blondel). When an excess of lime water is added to a solution of platinic chloride and the mixture exposed to sunlight, a white or yellowish pulverulent precipitate falls down, to which the name of calcium platinate has been given,[3] its composition corresponding approximately to the formula $CaPt_2O_5,CaCl_2,7H_2O$. If the hydroxide is boiled with a solution of a polymolybdate, or a polytungstate, salts are formed of the complex acids, platinmolybdic acid, $H_8PtMo_{10}O_{36}$, and platintungstic acid, $H_8PtW_{10}O_{36}$. These acids and their salts have a yellow or greenish colour, and are crystalline.[4]

Platino-platinic Oxide, Pt_3O_4, is obtained as a black insoluble powder by heating sodium platinichloride with sodium carbonate and extracting with water,[5] whilst *platinum sesquioxide*, Pt_2O_3, is obtained as a dark-brown powder [6] by heating spongy platinum with sodium dioxide, neutralising the alkali, washing, and drying at 450°. According to Wöhler, however, these substances are not definite oxides; only two oxides of platinum

[1] Bellucci, *Atti R. Accad. Lincei*, 1903, [5], **12**, ii., 635; Wöhler, *Zeit. anorg. Chem.*, 1904, **40**, 423; compare Blondel, *Ann. Chim. Phys.*, 1905, [8], **6**, 81.

[2] Bellucci and Parravano, *Atti R. Accad. Lincei*, 1905, [5], **14**, i. 459.

[3] Herschel, *Phil. Mag.*, 1832, [2], **1**, 58.

[4] Gibbs, *Ber.*, 1877, **10**, 1384.

[5] Jörgensen, *J. pr. Chem.*, 1877, [2], **16**, 344.

[6] Dudley, *Amer. Chem. J.*, 1902, **28**, 59.

exist and these readily form colloidal solutions and retain foreign matter on precipitation.

Platinum Trioxide, PtO_3, is obtained by the electrolysis of a solution of platinic hydroxide in 2N-potassium hydroxide. A compound of the composition $K_2O,3PtO_3$ is thus obtained, which, when treated with cold acetic acid yields the trioxide as a brown powder. It readily loses oxygen and slowly evolves chlorine from dilute hydrochloric acid.[1]

Platinum and the Halogens.

641 *Platinous Fluoride*, PtF_2, is formed when platinum wire is heated to dull redness in a current of fluorine. It is thus obtained as a deep-red coloured mass, which is very hygroscopic, and is decomposed by water slowly in the cold, more rapidly on heating. When the anhydrous substance is heated, it yields fluorine and leaves crystalline platinum.[2]

Phosphorus pentafluoride acts on spongy platinum at a red heat to form volatile crystals of the formula PF_3,PtF_2.[3]

Platinum Monochloride, PtCl.—When a solution of potassium platinichloride in 10,000 parts of water is heated for some days, a yellow, non-crystalline precipitate is formed which probably consists of hydrated platinum monochloride,[4] PtCl.

Platinous Chloride or *Platinum Dichloride*, $PtCl_2$, is formed when platinichloric acid, H_2PtCl_6, obtained by dissolving the metal in aqua regia and crystallising, is heated to 300°, or when spongy platinum is heated in a current of dry chlorine to between 240° and 250°.[5] It is a greenish-grey powder, having a specific gravity of 5·87, which is not readily moistened with water, and is insoluble in this liquid. On heating it decomposes into platinum and chlorine.[6]

Platinum dichloride unites with phosphorus trichloride to form the compound $PtCl_2,PCl_3$, which is obtained by heating spongy platinum with pentachloride of phosphorus to 250°. The product is easily soluble in benzene or chloroform, and crystallises therefrom in fine brown needles. When these are dissolved in water and the solution is evaporated in a vacuum,

[1] Wöhler and Martin, *Ber.*, 1909, **42**, 3326.
[2] Moissan, *Compt. rend.*, 1889, **109**, 807.
[3] Moissan, *Bull. Soc. chim.*, 1891, [3], **5**, 454.
[4] Sonstadt, *Proc. Chem. Soc.*, 1898, 25.
[5] Schützenberger, *Ann. Chim. Phys.*, 1870, [4], **21**, 351.
[6] See Shenstone, *Journ. Chem. Soc.*, 1892, **61**, 450.

orange-yellow deliquescent prisms of *chloroplatinophosphorous acid*, $PtCl_2,P(OH)_3$, are obtained. This has an acid metallic taste, and yields a white precipitate with silver nitrate and a yellow one with lead acetate. Corresponding salts of the alkali metals have not been prepared, since hydroxides and carbonates decompose the acid.

The foregoing compound readily takes up another molecule of phosphorus trichloride, forming $PtCl_2(PCl_3)_2$, which may likewise be crystallised from chloroform or benzene in large deliquescent prisms; these melt at 160°, and when strongly heated give off phosphorus trichloride. If they are allowed to remain in contact with water at a winter temperature, or if their solution be evaporated at a low temperature in a vacuum, very deliquescent yellow needles are obtained of *chloroplatinodiphosphorous acid*, $PtCl_2,2P(OH)_3$, and this readily undergoes decomposition at 12°, with evolution of hydrogen chloride, into the compound $PtClOP_2(OH)_5$. This latter forms white crystals, is less deliquescent than the former compounds, and when heated to 150° is converted into a light-yellow non-deliquescent powder having the composition $PtClO_2P_2(OH)_3$. The solution of this compound, like the preceding, is precipitated by silver nitrate.[1]

Carbonyl Platinochlorides or *Chloroplatinites.*—When platinous chloride is heated to a temperature of 250° in a current of carbon monoxide the following compounds are formed: $PtCl_2,2COCl_2$, $PtCl_2,CO$, $PtCl_2,2CO$, $2PtCl_2,3CO$. The last named is produced in largest quantity and is obtained in the pure state by boiling the crude product with carbon tetrachloride. In this way fine orange-yellow needles melting at 130° are obtained, and these when heated to from 250° to 260° in dry carbon dioxide yield the compound $PtCl_2,CO$ in fine needles; these melt at 194° and may be partially sublimed in a current of dry carbon dioxide at 240°, and at 300° decompose into carbonyl chloride, $COCl_2$, and platinum. When this compound, or the crude product, is heated to 150° in carbon monoxide, the compound, $PtCl_2,2CO$, sublimes in white needles which melt at 142°.[2] All these compounds are decomposed by water with separation of the metal and formation of carbon dioxide and hydrochloric acid.

[1] Schützenberger, *Bull. Soc. chim.*, 1872, [2], **17**, 482; **18**, 153; Rosenheim and Löwenstamm, *Zeit. anorg. Chem.*, 1903, **37**, 394.

[2] Schützenberger, *Ann. Chim. Phys.*, 1868, [4], **15**, 100, and 1870, **21**, 325; Pullinger, *Journ. Chem. Soc.*, 1891, **59**, 598.

642 *The Platinochlorides* or *Chloroplatinites.*—The solution of platinous chloride in hydrochloric acid may be regarded as *platinochloric* or *chloroplatinous acid,* $H_2[PtCl_4]$. The potassium salt is the usual starting point for the preparation of this compound and its salts.[1]

Potassium Platinochloride, K_2PtCl_4.—This salt, which was first prepared by Magnus,[2] is easily obtained by adding moist cuprous chloride to a thick paste of potassium platinichloride, $K_2,PtCl_6$, and water, in such quantity that a small portion remains unreduced. On cooling the filtered liquid, the greater portion of the platinochloride separates out, the mother-liquor yielding a second crop on concentration, whilst the remainder of the salt is precipitated from the last portion of the liquor with alcohol. These various crops are then washed with alcohol, and the pure salt is obtained by recrystallisation from hot water. It forms soft rose-coloured crystalline fibres. It may also be prepared by reducing a hot solution of platinichloric acid with sulphur dioxide until a sample gives no precipitate with ammonium chloride, and then adding a hot solution of potassium chloride. On cooling, potassium platinochloride separates out and is washed with alcohol and dried in absence of light.[3] When the requisite quantity of platinichloric acid is added to the hot saturated solution of this salt a precipitate of potassium platinichloride is formed and an almost pure solution of platinochloric acid, H_2PtCl_4, is obtained. The same acid is produced by treating the barium salt with dilute sulphuric acid. On evaporation in a vacuum over sulphuric acid or caustic potash. a solid compound separates out which dries with loss of hydrogen chloride, forming a brown amorphous mass of $H_2Pt(OH)Cl_3,H_2O$.[4] By dissolving oxides, hydroxides, carbonates or chlorides in the acid a series of compounds is obtained which has been fully described by Nilson.

Ammonium Platinochloride, $(NH_4)_2PtCl_4$.—This salt was described first by Vauquelin and afterwards by Peyronne. It crystallises from solution in hot water in large red four-sided prisms or in thin tablets.

Most of the other platinochlorides crystallise with water in fine red or brown crystals which are often deliquescent; some,

[1] Thomsen, *J. pr. Chem.*, 1877, [2], **15**, 294.
[2] *Pogg. Ann.*, 1828, **14**, 241.
[3] Klason, *Ber.*, 1904, **37**, 1360.
[4] Nilson, *J. pr. Chem.*, 1877, [2], **15**, 260.

such as the silver salt, Ag_2PtCl_4, and the lead salt, $PbPtCl_4$, are flesh-coloured precipitates.

Platinic Chloride or *Platinum Tetrachloride*, $PtCl_4$.—When metallic platinum is heated in a current of chlorine it is attacked, and this compound is slowly formed. The action diminishes when the temperature is raised, as the tetrachloride decomposes into metal and chlorine at 500°. If, however, the temperature be raised to 1,300°, the formation of tetrachloride recommences; and if an excess of chlorine be employed and the temperature raised to 1,700°, the action becomes rapid and a yellow sublimate of tetrachloride is deposited.[1] The same reaction occurs if a spiral platinum wire be heated by an electric current nearly to its melting point in a stream of chlorine. At the thick end of the wire crystals of metallic platinum are deposited. These are not formed owing to any volatility of the metal, but are produced by the alternate production and decomposition of the tetrachloride.[2] The anhydrous chloride is formed also when crystalline platinichloric acid is dried over sulphuric acid and then heated to 369° in a current of chlorine,[3] or at 165° in a current of hydrogen chloride.[4]

By mixing solutions of aqueous platinichloric acid and silver nitrate in the proportion of one molecule of the former to two of silver nitrate, a precipitate of silver platinichloride is thrown down, which is decomposed by hot water into silver chloride and platinic chloride. The yellowish-red solution yields on evaporation over sulphuric acid fine red, apparently monoclinic, crystals of the composition $PtCl_4,5H_2O$. They are not deliquescent, and their concentrated solution is only slowly precipitated by ammonium chloride on standing.[5] The crystals are converted by ammonia into the acid $PtCl(OH)_3$.[6] According to Miolati, platinum tetrachloride in aqueous solution is present as the dibasic acid $H_2PtCl_4(OH)_2$, and salts have been prepared corresponding to this acid, which are amorphous powders.[7]

[1] Troost and Hautefeuille, *Compt. rend.*, 1887, **84**, 946; Langer and Meyer, *Pyrochem. Untersuchungen*, p. 57.

[2] Hodgkinson and Lowndes, *Nature*, 1888, **38**, 6.

[3] Pigeon, *Compt. rend.*, 1890, **110**, 77; 1891, **112**, 1218; *Ann. Chim. Phys.*, 1894, [7], **2**, 433.

[4] Pullinger, *Journ. Chem. Soc.*, 1892, **61**, 422.

[5] Norton, *Journ. Chem. Soc.*, 1872, **25**, 680.

[6] Jörgensen, *J. pr. Chem.*, 1877, [2], **16**, 345.

[7] *Zeit. anory. Chem.*, 1900, **22**, 445; see also Kohlrausch, *Zeit. physikal. Chem.*, 1900, **33**, 257.

Hydrates containing one, four, and seven molecules of water have also been prepared.

Platinichloric Acid or *Chloroplatinic Acid*, $H_2[PtCl_6]$.—This compound, which is often erroneously called platinum chloride, is obtained by dissolving the metal in aqua regia and evaporating with hydrochloric acid until all nitric acid is removed. It crystallises in brownish-red, very deliquescent prisms having the composition $H_2PtCl_6,6H_2O$. If the solution be repeatedly evaporated with aqua regia, nitrosoplatinic chloride, $(NO)_2PtCl_6$, is formed. This crystallises in small orange-coloured cubes and is very deliquescent, dissolving in water with evolution of nitric oxide.

The hydrogen in platinichloric acid can be readily replaced by metals, and thus a series of crystalline salts termed the *platinichlorides* or *chloroplatinates* is obtained, of which the most important are those of the alkali metals, their widely differing solubilities rendering them very valuable in analytical chemistry.

Potassium Platinichloride or *Potassium Chloroplatinate*, K_2PtCl_6, is thrown down, on the addition of potash or a potassium salt to the acid, in the form of a yellow crystalline precipitate which is deposited from solution in hot water in the form of small reddish-yellow octahedra, having a specific gravity of 3·586. One hundred parts of water dissolve, according to Bunsen and Kirchoff, as follows:

At 0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
0·70	0·90	1·12	1·41	1·76	2·17	2·61	3·19	3·79	4·45	5·18 parts.

It is insoluble in a saturated solution of potassium chloride as well as in alcohol. It dissolves in caustic potash and is precipitated from the solution on the addition of acids.

Sodium Platinichloride, $Na_2PtCl_6,6H_2O$, is obtained by evaporating the acid with common salt, when light red triclinic prisms or tablets are deposited which have a specific gravity of 2·499. These become anhydrous at 100°, falling to a yellowish-red powder, which is readily soluble in water and alcohol.

Lithium Platinichloride, $Li_2PtCl_6,6H_2O$, crystallises in large orange-yellow plates which effloresce in the air and are easily soluble in water and in a mixture of alcohol and ether, but not in pure ether.

Rubidium Platinichloride, Rb_2PtCl_6, closely resembles the

potassium salt, but is still less soluble, 100 parts of water dissolving, according to Bunsen, the following amounts:

At 20°	40°	60°	80°	100°
0·141	0·166	0·258	0·417	0·634 part.

Cæsium Platinichloride, Cs_2PtCl_6, is the least soluble of the platinichlorides of the alkali metals, 100 parts of water dissolving:

At 20°	40°	60°	80°	100°
0·070	0·142	0·213	0·291	0·377 part.

It forms, like the rubidium salt, microscopic glistening honey-yellow transparent octahedra.

Ammonium Platinichloride, $(NH_4)_2PtCl_6$, is obtained by precipitating the acid with an ammonium salt, as a lemon-yellow crystalline powder, which crystallises from hot water in orange-yellow octahedra; these have a specific gravity of 3·0, and are indistinguishable in appearance from the potassium salt. One hundred parts of water dissolve at the ordinary temperature about 0·666, and at 100° 1·25 parts of the salt. It is not soluble either in alcohol or ether, and scarcely soluble in a solution of ammonium chloride. On heating it decomposes without fusion, leaving pure platinum sponge behind. Other acids and their corresponding salts have been prepared which may be regarded[1] as being intermediate between platinic acid, $H_2[Pt(OH)_6]$, and platinichloric acid, $H_2[PtCl_6]$, and to these compounds may be ascribed formulae such as $H_2[Pt(OH)_5Cl]$ and $H_2[PtCl_5(OH)]$.

Platinous Bromide, $PtBr_2$, is obtained by heating platinibromic acid to 280°, and forms a brown mass which dissolves with a brownish-red colour. If boiling saturated solutions of potassium platinichloride and potassium bromide are mixed, double decomposition occurs, and the potassium chloride may be separated from the *potassium platinobromide*, K_2PtBr_4, by crystallisation. The latter forms large, nearly black pyramids or brownish-red needles (Thomsen). Like the chloride it unites with carbon monoxide, forming a compound, $PtBr_2,CO$ (Pullinger).

Platinic Bromide, $PtBr_4$.—Bromine acts upon platinum at different temperatures in the same way as chlorine. The tetra-

[1] Miolati and Bellucci, *Atti R. Accad. Lincei*, 1900, [5], **9**, ii., 140; 1903, [5], **11**, ii., 241, 271.

bromide is best obtained by heating spongy platinum with bromine and hydrobromic acid to 180°, evaporating the solution and drying the residue at 180°. It is a brownish-black deliquescent powder, nearly insoluble in water, but readily soluble in alcohol and ether, yielding a brown solution.[1] When platinum is dissolved in a mixture of nitric and hydrobromic acids, and the concentrated solution allowed to evaporate over quick lime, dark-red monoclinic prisms of *platinibromic acid*, $H_2PtBr_6,9H_2O$, are deposited, which are very deliquescent. This compound gives rise to a series of platinibromides corresponding to the platinichlorides, most of which possess a red colour.

Platinous Iodide, PtI_2, is formed by warming the chloride with a solution of potassium iodide. It is also formed with liberation of iodine when excess of potassium iodide is added to a solution of potassium platinichloride, and this reaction has been used as a method of estimating platinum.[2] It is a black powder closely resembling lamp-black in appearance.

Platinic Iodide, PtI_4, is a black or brownish-black amorphous powder obtained by the action of hydriodic acid on a soluble platinichloride. *Platiniodic acid*, $H_2PtI_6,9H_2O$, easily decomposes into water, hydriodic acid, and platinic iodide. The *platiniodides* are brown, and possess a metallic lustre; they are soluble in water, and are very unstable, giving off iodine at a temperature below 100°.

Platinum and the Elements of the Sulphur Group.

643 *Platinum Monosulphide*, PtS, is formed when platinum sponge is heated with sulphur in a vacuous glass tube, or when platinous chloride is fused with sodium carbonate and sulphur, and the mass extracted with water. It forms a green powder or a mass of glistening needles.[3] When heated in the air it decomposes, leaving a residue of platinum, and when ignited in hydrogen it yields sulphuretted hydrogen and spongy platinum.

Platinum Disulphide, PtS_2, is formed as a steel-grey powder by heating ammonium platinichloride with sulphur to a dark-

[1] V. Meyer and Züblin, *Ber.*, 1880, **13**, 404; Halberstadt, *ibid.*, 1884, **17**, 2962.

[2] Peterson, *Zeit. anorg. Chem.*, 1898, **19**, 59.

[3] Debray and Deville, *Compt. rend.*, 1879, **89**, 587.

red heat. When sulphuretted hydrogen is passed through a solution of a platinic salt a black precipitate of sulphide is first formed, but this by further action of the gas becomes light-brown, from formation of hydrogen platinum sulphide, a compound which on exposure to the air again gives off sulphuretted hydrogen.

The disulphide may be obtained pure by precipitating a solution of potassium platinichloride at 90° with sulphuretted hydrogen, and drying at 70–80° in an atmosphere of nitrogen.[1]

Platinum disulphide combines with basic sulphides and therefore dissolves in the sulphides of the alkali metals.

Potassium Platinothioplatinate, $K_2Pt_4S_6 = K_2S,3PtS,PtS_2$, is obtained by fusing together platinum sponge, potash, and sulphur, and lixiviating the mass with water. It then separates in the form of hard six-sided tablets, which on heating in the air burn like tinder. Dilute sulphuric acid converts it into $H_2Pt_4S_6$, and this on exposure to air oxidises to *platinum sesquisulphide*, Pt_2S_3, forming a steel-grey crystalline powder.

Di-sodium Platinothioplatinate, $Na_4Pt_3S_6 = 2Na_2S,2PtS,PtS_2$, is obtained in a similar way to the preceding compound, and forms pale copper-red thin crystalline needles which are converted in contact with hydrochloric acid, without alteration of form, into a reddish-brown compound, $H_4Pt_3S_6$, which oxidises extremely quickly in the air with formation of the sesquisulphide.[2]

A compound of the formula $PtS_{15}(NH_4)_2,2H_2O$ has been prepared by the action of ammonium polysulphide on platinichloric acid,[3] and forms large red rhombic crystals.

Potassium Platinosulphite, $K_6Pt(SO_3)_4,2H_2O$.—A solution of potassium platinochloride becomes decolorised when warmed with acid potassium sulphite, the above salt separating out from the solution in yellowish or colourless needles. Sodium salts precipitate from this solution *sodium platinosulphite*, $Na_6Pt(SO_3)_4$, $7H_2O$, in microscopic needles. *Ammonium platinosulphite*, $(NH_4)_6Pt(SO_3)_4$, is obtained by similar means.

These compounds must be regarded as salts of complex acids, since they do not show the ordinary reactions for either platinum or sulphurous acid.

Platinic Sulphate, $Pt(SO_4)_2$, is obtained as a brown mass by

[1] Antony and Lucchesi, *Gazz.*, 1896, **26**, i., 211.
[2] Schneider, *Pogg. Ann.*, 1866, **138**, 604.
[3] Hofmann and Höchtlen, *Ber.*, 1903, **36**, 3090.

acting on the hydroxide or chloride with sulphuric acid and evaporating the solution.

Platinum Selenide.—Spongy platinum unites with selenium with incandescence when these substances are heated together, with formation of a grey infusible powder; this, when heated before the blowpipe, loses the whole of its selenium. Platinum also unites with tellurium [1] to form the tellurides, Pt_2Te, PtTe, and $PtTe_2$.

Platinum and the Elements of the Nitrogen Group.

644 *The Platinonitrites* or *Nitrito-platinites.*—These compounds are probably analogous in composition to the ammoniacal derivatives corresponding to the platinous salts (p. 1399), and behave not as double salts, but as salts of a complex acid, since they do not show the usual reactions either of platinum salts or nitrites. They were first described by Lang,[2] and afterwards investigated more completely by Nilson.[3]

Potassium Platinonitrite, $K_2Pt(NO_2)_4$, is obtained when solutions of potassium nitrite and potassium platinochloride are warmed together. It is deposited in the form of small glistening six-sided prisms, which dissolve in 27 parts of water at 15°, and at a higher temperature in a smaller quantity. Alkalis do not precipitate platinum oxide, and sulphuretted hydrogen does not precipitate sulphide of platinum from its solution. When the solution is allowed to evaporate spontaneously, rhombic tablets having the composition $K_2Pt(NO_2)_4,2H_2O$ separate out, which effloresce rapidly. It readily combines with a molecule of chlorine or bromine,[4] and forms with dry liquid nitrogen peroxide the compound $K_2Pt(NO_2)_4,N_2O_4$, and with cool concentrated hydrochloric acid the compound $K_2Pt(NO_2)_4,HCl$.[5]

Silver Platinonitrite, $Ag_2Pt(NO_2)_4$, is obtained when solutions of the potassium salt and silver nitrate are mixed. On recrystallising the precipitated salt from hot water, large yellow glistening monoclinic prisms are obtained, which on heating decompose with incandescence and detonation.

[1] Roesslèr, *Zeit. anorg. Chem.*, 1897, **25**, 405.
[2] *J. pr. Chem.*, 1861, **83**, 415. [3] *Ber.*, 1876, **9**, 1722; 1877, **10**, 934.
[4] Blomstrand, *J. pr. Chem.*, 1871, [2], **3**, 207; Vèzes, *Compt. rend.*, 1891, **112**, 616; **113**, 696.
[5] Miolati, *Atti R. Accad. Lincei*, 1896, [5], **5**, ii., 355.

Barium Platinonitrite, $BaPt(NO_2)_4,3H_2O$, is obtained by decomposing the silver salt with barium chloride. It crystallises from solution in hot water in colourless octahedra. If this salt be decomposed by dilute sulphuric acid, and the solution evaporated in a vacuum over caustic potash, microscopic crystals having the colour of chromium trioxide separate out; these possess, according to Lang, the composition $H_2Pt(NO_2)_4$. Nilson, however, was unable to obtain this compound. The solution yielded, on evaporation, a gummy mass and a green glistening residue, having the composition $H_4Pt_3O(NO_2)_8,2H_2O$, and this, on neutralisation with potash and evaporation, yielded the potassium salt, $K_4Pt_3O(NO_2)_8,2H_2O$, in oblique four-sided glistening light-yellow tablets.

Fulminating Platinum.—E. v. Meyer has examined a series of explosive compounds obtained by acting upon ammonium platinichloride with potash, the existence of some of which was pointed out long ago by Proust and Döbereiner. Their constitution is as yet unknown; the yellow precipitate obtained on heating ammonium platinichloride with potash has the composition $PtClNH_6O_2$.[1]

Ammoniacal Platinum Compounds.

645 As already stated (p. 1348), the various platinum salts are capable of forming complex compounds with ammonia. The first of these compounds was obtained in 1828 by Magnus[2] by the action of ammonia on platinous chloride as a green insoluble salt having the empirical composition $PtCl_2(NH_3)_2$, which is usually known as Magnus' green salt. Gros[3] then obtained a series of light-yellow or colourless salts by the action of nitric acid upon the green salt of Magnus. Reiset[4] and Peyronne[5] independently found that by the action of ammonia on Magnus' green salt, or on platinous chloride, two other series of compounds could be obtained. These were distinguished as the chlorides of Reiset's first and second bases. Peyronne showed that Magnus' salt is a platinichloride

[1] *J. pr. Chem.*, 1878, [2], **18**, 305.
[2] *Pogg. Ann.*, 1828, **14**, 204.
[3] *Ann. Chim. Phys.*, 1838, [2], **69**, 204.
[4] *Ann. Chim. Phys.*, 1844, [3], **11**, 417; *Compt. rend.*, 1840, **10**, 870; 1844, **18**, 1103.
[5] *Ann. Chim. Phys.*, 1844, [3], **12**, 193; 1846 [3], **16**, 462.

of the second base. Further investigations of these compounds, and theoretical speculations concerning their constitution, have been made by various other chemists.[1]

The constitution of these compounds is probably similar to that of the chromium bases, and has been similarly interpreted, according to each of the two views already discussed (p. 1051). These derivatives exist in two series, in which the platinum is divalent and tetravalent respectively.

In the platinous series, the metal is capable of combining with or co-ordinating only 4 molecules or radicals to form the characteristic complex radical, and the maximum number of external acid radicals is 2, since the platinum is divalent.

In the platinic series, on the other hand, the metal, like chromium, is capable of forming a complex radical with 6 molecules or radicals, but, platinum being in these salts tetravalent, the maximum number of external acid radicals is 4, instead of 3 as in the derivatives of trivalent chromium.

It is characteristic of the platinum series that the free hydroxides from which the salts are derived are in many cases stable substances, whereas this is rarely the case in the chromium and cobalt series.

The following are the chief series of these derivatives which have been described, X and R being monovalent acid and basic radicals respectively.

Platinous Compounds.

1. Tetrammine-platinous compounds, $[(NH_3)_4Pt]X_2$.
   (Plato-diammine.)
2. Triammine-platinous compounds, $[X(NH_3)_3Pt]X$.
3. Diammine-platinous compounds, $[X_2(NH_3)_2Pt]$.
   (Platosammine and platosemidiammine.)
4. Monammine-platinous compounds, $[X_3(NH_3)Pt]R$.
   (Platosemiammine.)

[1] Raewsky, *Ann. Chim. Phys.*, 1844, [3], **12**, 278; Gerhardt, *Compt. rend.*, 1850, **31**, 244; Buckton, *Annalen*, 1852, **84**, 220; Thomsen, *Ber.*, 1870, **3**, 42; Odling, *Ber.*, 1870, **3**, 42; Blomstrand, *Ber.*, 1871, **4**, 673; Cleve, *Bull. Soc. chim.*, 1867, [2], **7**, 12; 1871, **15**, 161; **16**, 203; 1872, **17**, 289; Cossa, *Journ. Chem. Soc.*, 1887, **52**, 642; 1896, **70**, ii., 251; *Ber.*, 1890, **23**, 2503; *Zeit. anorg. Chem.*, 1891, **1**, 65; Werner, *ibid.*, 1893, **3**, 267; 1895, **8**, 153; 1896, **12**, 46; see also references given under chromium (p. 1055).

Platinic Compounds.

1. Hexammine-platinic compounds, $[(NH_3)_6Pt]X_4$. (Drechsel's base.)
2. Pentammine-platinic compounds; unknown.
3. Tetrammine-platinic compounds, $[X_2(NH_3)_4Pt]X_2$. (Platin-diammine.)
4. Triammine-platinic compounds, $[X_3(NH_3)_3Pt]X$. (Platinmonodiammine.)
5. Diammine-platinic compounds, $[X_4(NH_3)_2Pt]$. (Platinammine and platinsemidiammine.)
6. Monammine-platinic compounds, $[X_5(NH_3)Pt]R$. (Platinisemiammine.)

Magnus' Green Salt $[(NH_3)_4Pt]\,[PtCl_4]$, which is the starting-point for the preparation of these derivatives, is made by the action of ammonia on platinous chloride, and when boiled with ammonia passes into *tetrammine-platinous chloride*, $[(NH_3)_4Pt]Cl_2$.

The tetrammine salts lose ammonia when heated, thus yielding the symmetrical diammine compounds (platosammine salts), whilst the isomeric asymmetrical compounds (platosemidiammine salts) are formed by the moderate action of ammonia on the platinous salts. The platinic salts are formed by the oxidation of the corresponding platinous derivatives. The diammine compounds of both the platinous and platinic series can exist in two geometrically isomeric forms, as previously explained (p. 1053).

In addition to the classes of compounds already mentioned, several others have been described containing organic substituted ammonias in the complex radical, and also compounds the members of which contain more than one atom of platinum. Very little is known of these latter compounds, for a detailed description of which reference must be made to the original papers.

Platinum and Phosphorus and Arsenic.

646 *Platinum and Phosphorus.* — These two elements fuse together readily. If finely divided platinum be heated in the vapour of phosphorus it burns with evolution of light to form *platinum diphosphide*, PtP_2, which is a bright mass with a metallic lustre, not attacked by hydrochloric acid, but easily

dissolved by ammonia (Schrötter). According to Granger[1] the phosphide Pt_3P_5 is formed at the same time, and this compound is also obtained if platinum be heated at about 600° in phosphorus vapour.

Spongy platinum and arsenic unite with incandescence. The brittle alloy, $PtAs_2$, loses the whole of its arsenic on ignition. Platinum forms brittle alloys also with antimony, bismuth, and vanadium.

Platinum and Carbon.

647 *The Platinocyanides.*—The potassium salt is formed when a mixture of equal parts of spongy platinum and potassium ferrocyanide is heated nearly to redness in a crucible, the mass dissolved in water, and the filtrate evaporated (Gmelin), or when platinous chloride is dissolved in potassium cyanide.[2] The other salts can be obtained by double decomposition.

Platinocyanic Acid, $H_2[PtCy_4]$, is obtained by decomposing the copper or mercury salt with sulphuretted hydrogen,[3] or by decomposing the barium salt with dilute sulphuric acid.[4] After evaporating to dryness, the residue is treated with a mixture of alcohol and ether, and the ethereal solution allowed to evaporate spontaneously, when fine cinnabar-red prisms, exhibiting a splendid blue colour by reflected light, are obtained. These have the composition $H_2PtCy_4,5H_2O$. Sometimes yellowish-green crystals, having a copper-red or golden lustre, are obtained, which contain more water. When heated to 100° they become yellow, and they decompose at temperatures above 140°. They are deliquescent, yielding a colourless solution in alcohol; the aqueous solution decomposes carbonates with evolution of carbon dioxide.

Potassium Platinocyanide, $K_2PtCy_4,12H_2O$, is obtained by dissolving ammonium platinichloride together with caustic potash in a boiling concentrated solution of potassium cyanide. The liquid is boiled until no further evolution of ammonia takes place, when the salt crystallises out.[5] This is also formed when spongy platinum is boiled with a solution of potassium cyanide, or when a mixture of these two substances is heated

[1] *Compt rend.*, 1896, **123**, 1284.
[2] Knop, *Annalen*, 1842, **43**, 111.
[3] Quadrat, *Annalen*, 1847, **63**, 164; 1848, **65**, 249; 1849, **70**, 300.
[4] Weselsky, *J. pr. Chem.*, 1856, **69**, 276.
[5] Martius, *Annalen*, 1861, **117**, 357.

at a temperature of from 500° to 600° in steam (Deville and Debray):

$$4KCy + Pt + 2H_2O = K_2PtCy_4 + 2KOH + H_2.$$

It forms long, yellow, rhombic prisms, exhibiting a blue metallic lustre by reflected light, and it is very readily soluble in water. If the hot solution be saturated with chlorine, or boiled with aqua regia, colourless prisms of *potassium chloroplatinicyanide*, $K_2PtCy_4Cl_2,2H_2O$, are obtained on evaporation. If this solution be mixed in the right proportion with potassium platinocyanide a double salt is obtained of the composition $5K_2PtCy_4,K_2PtCy_4Cl_2,21H_2O$, crystallising in magnificent green prisms which exhibit a copper-red lustre by reflected light and are soluble in water. This salt, which is formed also when potassium platinocyanide is treated with a moderate quantity of chlorine, was at one time believed to be a platinicyanide corresponding to potassium ferricyanide, as the presence of chlorine in it had been overlooked, and because in alkaline solution it acts as an oxidising agent, potassium hypochlorite being formed:

$$5K_2PtCy_4 + K_2PtCy_4Cl_2 + 2KOH = 6K_2PtCy_4 + KOCl + KCl + H_2O.$$

Its true composition was first pointed out by Hadow.[1]

Barium Platinocyanide, $BaPtCy_4,4H_2O$, was first obtained by passing hydrocyanic acid into water containing platinous chloride and barium carbonate in suspension.[2] It can also be readily obtained by decomposing the copper salt by baryta water, or by adding the calculated quantity of barium hydroxide and hydrocyanic acid to a solution of platinichloric acid, and treating the warm mixture with sulphur dioxide until colourless. The barium sulphate formed is filtered off and the solution cooled, when barium platinocyanide separates out and may be purified by recrystallisation from water. This method of preparation serves as a means of separating platinum from iridium, the compound of the latter metal remaining in solution.[3] Barium platinocyanide forms large rhombic crystals which exhibit a green colour in the direction of the primary axis,

[1] *Journ. Chem. Soc.*, 1861, 106.
[2] Weselsky, *J. pr. Chem.*, 1856, **69**, 276.
[3] Bergsöe, *Zeit. anorg. Chem.*, 1899, **19**, 318.

whilst at right angles to this direction they appear of a sulphur-yellow colour.

Magnesium Platinocyanide, $2MgPtCy_4,7H_2O$, is obtained by decomposing the barium salt with magnesium sulphate, and is one of the most beautiful salts of this group. It forms large square-based red prisms, the sides of which viewed by reflected light have a beetle-green lustre, whilst the end faces reflect blue or purple light. It crystallises from alcohol with six molecules of water in four-sided lemon-yellow tablets, having a blue reflection, and often exhibiting all shades of colour of red, blue, and green.

Many other platinocyanides besides these are known, of which several are remarkable for their splendid play of colours. Some, such as the green copper salt, are insoluble powders obtained as precipitates by double decomposition. A very characteristic reaction for the platinocyanides is that on addition of a mercurous or a mercuric salt to their solution a white precipitate is first thrown down, but on addition of more mercurous salt this becomes of a smalt-blue colour.

These salts become luminous when exposed to the Röntgen rays, and are employed for making screens by means of which the absorption of these rays may be observed.

Potassium Platinothiocyanate, $K_2Pt(SCN)_4$, is obtained by dissolving platinum dichloride in a solution of potassium thiocyanate, or, better, by dissolving equal parts of potassium platinochloride and potassium thiocyanate in the smallest quantity of water, when the mixture becomes warm, and, on cooling, the salt separates out in red microscopic prisms. When the corresponding barium salt is decomposed by dilute sulphuric acid, the free acid is obtained in solution, but this undergoes rapid decomposition.[1]

Platinithiocyanic Acid, $H_2[Pt(SCN)_6]$.—On decomposing the lead salt with dilute sulphuric acid, a thick dark-red very acid liquid is obtained, which decomposes carbonates, and dissolves zinc with evolution of hydrogen. On evaporation in a vacuum an indistinct crystalline mass remains behind.

Potassium Platinithiocyanate, $K_2Pt(SCN)_6$, is obtained by adding potassium thiocyanate solution, not in excess, to a solution of potassium platinichloride and heating to boiling. The filtered solution on cooling deposits large six-sided prisms or tablets having a carmine-red colour and possessing a very

[1] Buckton, *Journ. Chem. Soc.*, 1855, 22.

disagreeable taste. They dissolve in water forming such a deep-red solution that one drop of the concentrated liquid imparts a distinct colour to 100,000 parts of water. When the concentrated solution is boiled with ammonium sulphate a very similar ammonium platinithiocyanate is formed. The platinithiocyanates of the alkali metals are soluble in water and crystallisable; those of the heavy metals are insoluble, and have a yellowish- or blackish-red colour (Buckton).

Detection and Estimation of Platinum.

648 If a platinum compound be heated on a carbonised match in the gas-flame a grey spongy mass is obtained soluble only in aqua regia. The concentrated solution yields with potassium chloride and ammonium chloride the well-known and characteristic precipitates. Sulphuretted hydrogen throws down from solutions of a platinum salt, slowly in the cold but more quickly on heating, the brown disulphide which is soluble in an excess of yellow ammonium sulphide. A solution of stannous chloride colours platinic chloride solutions dark-brown, inasmuch as platinous chloride is formed.

In the general separation of the metals platinum and gold are obtained together with arsenic, antimony, and tin. Their presence is indicated by the brown colour of the precipitate produced by hydrochloric acid in the solution in ammonium sulphide. In this case the precipitate is fused with sodium carbonate and nitre, the fused mass lixiviated with water, and the residue, which may contain the gold and platinum together with tin dioxide and sodium antimonate, is treated with zinc and hydrochloric acid when the latter two compounds are reduced to metals. The mass is first boiled with hydrochloric acid to remove the tin, and next with nitric acid and a little tartaric acid to dissolve the antimony; the residue is then treated with aqua regia, the solution concentrated and evaporated to dryness on the water-bath with an excess of ammonium chloride, and alcohol added to dissolve the gold chloride. From the alcoholic solution the gold may be readily precipitated with ferrous sulphate. The portion insoluble in alcohol may contain ammonium platinichloride, and this on ignition will leave a residue of spongy platinum. The qualitative separation of the platinum metals by means of their sulphides has already been described (p. 1359).

An alternative method for the rapid qualitative analysis of a mixture containing these metals has been devised by Mylius and Dietz.[1] A solution of the chlorides is boiled in a retort with dilute nitric acid and the vapours passed into a solution of caustic soda. If osmium be present it is thus converted into the volatile tetroxide which forms a yellow solution in the soda and may be detected in the usual manner. The residual liquor, after extraction with ether to remove gold chloride, is then heated with ammonium acetate and formic acid for several hours in a reflux apparatus, whereby the salts of the platinum metals are reduced to the metals, and the black precipitate, after washing and drying, is heated to redness in a stream of hydrogen to remove mercury. The residue is then extracted with hydrochloric acid, mixed with sodium chloride, heated in chlorine and the product dissolved in a little water, filtered, and ammonium chloride added so long as any precipitate forms. In this way the platinum, iridium, and ruthenium are precipitated, whilst the palladium and rhodium remain in solution, but the separation is not quantitative. The precipitate is dissolved in warm water, treated with hydroxylamine and again precipitated with ammonium chloride, whereby the tetrachlorides of ruthenium and iridium first formed are converted into the trichlorides which remain in solution, whilst the platinum is precipitated as ammonium platinichloride. Ruthenium and iridium are separated in the filrate from this precipitate by evaporating to dryness, reducing to the metals in a current of hydrogen, fusing with potash and nitre, extracting with water and distilling off the volatile ruthenium tetroxide in a current of chlorine into dilute acidified alcohol. The iridium is detected in the insoluble residue by treatment with chlorine and sodium chloride and precipitation with ammonium chloride. The original filtrate containing rhodium and palladium is evaporated to dryness with excess of ammonia, the residue dissolved in the least possible quantity of ammonia and cooled, when the less soluble ammoniacal rhodium chloride separates out, and the palladium may be precipitated from the filtrate by hydrochloric acid as palladosammine chloride.

The *quantitative estimation* of platinum always takes place as metal, obtained by ignition of ammonium platinichloride, or by heating potassium platinichloride in a current of hydrogen and

[1] *Ber.*, 1898, **31**, 3191.

lixiviating the residue with water, or sometimes also by ignition of the sulphide.

The Atomic Weight of platinum was determined by Berzelius [1] by analysis of the potassium double chloride; the mean number obtained by him was 197·1; Andrews,[2] who employed the same method, found the atomic weight to be 197·9, but Seubert [3] obtained 195·14, and Halberstadt,[4] confirming this result, found 195·07. More recent work by Archibald,[5] who analysed the carefully purified potassium and ammonium salts of chloro- and bromo-platinic acids, has given the figure 195·23. The value now (1913) adopted is 195·2.

[1] *Lehrbuch*, 5te *Aufl.* **3**, 1212.
[2] *Chem. Gaz.*, 1852, 379.
[3] *Annalen*, 1881, **207**, 1.
[4] *Ber.*, 1884, **17**, 2963.
[5] *Proc. Roy. Soc. Edin*, 1909, **29**, 721.

THE RADIOACTIVE ELEMENTS.

649 Becquerel's discovery of the radioactivity of uranium in 1896 has led to the development of an entirely new branch of scientific thought. Special methods of investigation, mainly physical in character, have been invented, and the results are of extraordinary interest and importance. Much, however, yet remains to be done before many of the conclusions hitherto drawn can be considered as established, and discoveries are constantly being made. Under these circumstances only a very brief outline of the subject is here attempted.[1]

650 The phenomena of the electrical discharge in an ordinary vacuum tube containing gas at a few millimetres pressure are familiar to everyone. If the tube contain air or nitrogen, we have the negative pole, or cathode, clothed with a violet glow, quite distinct from the brick-red positive column, which occupies most of the tube. The narrow portion of the tube may be bent into any curved form—a spiral, for example—and the discharge follows all the curves. But the phenomena are quite different if the vacuum in the tube be greatly increased; the dark space which separates the cathode from the violet glow becomes much greater, and the discharge from the cathode refuses to follow convolutions of the tube, but pursues a straight course, normal to the surface of the cathode, until it strikes the glass, where it produces phosphorescence. The phenomena of such high vacua were investigated by Crookes[2] in 1870. He found these electric streams from the cathode to be capable of producing brilliant phosphorescence in diamonds, rubies, &c., and of throwing well-defined shadows of objects placed in their path upon the opposite wall of the tube, which

[1] A full account of the subject is given in *Radioactive Substances and their Radiations*, by Rutherford (Cambridge: The University Press, 1913). The chemical behaviour of radioactive bodies is dealt with by Soddy in *The Chemistry of the Radio-Elements* (Longmans).

[2] *Phil. Trans.*, 1874, **164**, 501; 1875, **165**, 519; 1876, **166**, 325.

phosphoresces all round the shadow. Further, this electric stream is capable of putting lightly poised vanes into motion, and it is deflected by a magnet brought near the tube. Such an electric stream is now spoken of as consisting of "cathode rays." It was shown by Hertz that the cathode rays, though they will not pass through glass or mica, will penetrate thin metal foil, and Lenard, by constructing vacuum tubes with aluminium "windows," observed the cathode rays to pass out through the metal into the air, and there to produce phosphorescence, although the rays cannot be produced at all in air at ordinary pressure. There is now no doubt that Crookes was right in speaking of these phenomena as belonging to a "fourth state" of matter, as something quite different from matter in either the solid, liquid, or gaseous state. The cathode rays are generally recognised as streams of electrons carrying negative charges.

J. J. Thomson showed,[1] in 1897, that the cathode rays are not only deflected in a magnetic field, but are also deflected by an electric field, and this is what should occur if the rays are streams of negatively electrified particles. This investigator employed an experimental arrangement consisting of a vacuum tube so arranged that the cathode stream passed midway between two parallel insulated plates of metal, which were respectively charged positively and negatively. When the plates were uncharged the cathode stream produced a luminous spot on the end of the tube, but when the plates were charged the displacement of the luminous spot showed that the stream had been deflected towards the positively charged plate, thus proving that the particles of which the stream consisted carried a negative charge.

By means of an electro-magnet the stream could be deflected in the opposite direction so as to bring the luminous spot back to its original position, and by measurement of the strengths of the electric and magnetic fields, data were obtained for calculating the velocity of the particles, and also the ratio of the electric charge to the apparent mass of a particle. The strength X of the electric field is V/d where V is the difference of potential of the plates, and d their distance apart. If H be the strength of the magnetic field, the force acting on a particle with charge e and moving with velocity u is Heu, and when a balance has been obtained,

[1] *Phil. Mag.*, 1897, [5], **44**, 293.

$$Heu = Xe. \quad . \quad . \quad . \quad (1)$$

If the magnetic field be acting alone, a particle of mass m and charge e describes a circular orbit of radius ρ, such that:

$$H\rho = \frac{mu}{e}. \quad . \quad . \quad . \quad (2)$$

From equations (1) and (2) the values of u and e/m can be determined. By measurements made in this way it has been found that the velocity of the particles varies between 10^9 and 10^{10} cm. per second. (The velocity of light is 3×10^{10}, and the velocity of the molecules of hydrogen in the gas at 0° C. is $1{\cdot}844 \times 10^5$ cm. per sec.). These experiments do not, however, give us the mass of a particle, but only the ratio of the charge to the mass. It follows from Faraday's laws of electrolysis that all monovalent ions in electrolysis carry the same charge, and experiment has shown that it requires $9{\cdot}6 \times 10^3$ electro-magnetic units of electricity to set free one gram of hydrogen. If N be the number of atoms in one gram of hydrogen, then $Ne = 9{\cdot}6 \times 10^3$, and if m be the mass of a hydrogen atom, then $Nm = 1$. Hence $e/m = 9{\cdot}6 \times 10^3$ for the hydrogen ion. Simon [1] obtained an average value of $1{\cdot}86 \times 10^7$ (with an average velocity of 7×10^9) for the ratio e/m for the cathode rays, and if we assume that the charge of the particles (or electrons) is the same as that of an atom of hydrogen, so that e has the same value in the two equations $e/m = 1{\cdot}86 \times 10^7$ and $e/m' = 9{\cdot}6 \times 10^3$ (where m' is the mass of the hydrogen atom), then $m' = 1943m$. The mass of the particle in the cathode rays is thus about the one two-thousandth part of the mass of a hydrogen atom.

It has been mentioned that the cathode rays excite phosphorescence in the glass of the tube at the place where they impinge, or in other substances placed in the path of the stream of electric particles.

In 1895 Röntgen discovered that under these circumstances the phosphorescent glass emitted rays of a most remarkable character—the so-called X-rays—capable of penetrating such opaque substances as paper, wood, aluminium, flesh, &c., but stopped by lead, platinum, glass, or bone. These rays have the power of exciting fluorescence in such substance as barium platinocyanide, and of affecting a photographic plate; so that it

[1] *Ann. Physik*, 1899, **69**, 589.

is possible to photograph, or by the use of a fluorescent screen to see, the shadow of the bones in one's hand, or a coin concealed between the pages of a book. The X-rays are incapable of refraction or reflection from isotropic media; recently, however, reflections have been obtained from crystalline substances such as mica, but this phenomenon is probably more analogous to interference in optics than to true reflection.[1] The rays are not sensibly acted on by a magnet. They have also been found to have the power of discharging an electroscope.

There is another type of rays which is observed when an electric discharge passes through a rarefied gas. It was shown by Goldstein that under certain conditions of pressure, streams of rays pass through the holes in a perforated cathode. These streams are known as canal rays, and have been shown by Wien to consist of positively charged particles moving with high velocities. From measurements of their deflection in electric and magnetic fields, it appears that the carriers of the electricity are of atomic size and thus differ in this respect from the cathode particles, as well as in carrying electricity of opposite sign. This distinction between the sizes of the carriers of positive and negative electricity is general and of great importance, and will be seen later to exist in the positively and negatively charged radiations emitted by radioactive bodies.

Some recent experiments by J. J. Thomson are of particular interest as a delicate means of chemical analysis. The method consists in subjecting the positive rays simultaneously to an electric and magnetic field and noting the deflection suffered by the rays. The electric and magnetic fields are arranged to be in the same direction so as to deflect the rays in two directions at right angles to each other, with the result that the particles move along different paths determined by the masses and velocities of the particles. The experimental arrangement will be understood from Fig. 203. An electric discharge is passed through the rarefied gas contained in the vessel A provided with a cathode C with a small hole at its centre. The positively electrified particles which move with great velocity towards the cathode pass through this hole and emerge as a fine pencil of electrified particles passing between the plates L and M connected to the positive and negative poles of a battery, and between the pole-pieces P and Q

[1] Laue, Friedrichs, and Knipping, *Sitzungsber. Bayr. Akad. Wiss.*, 1912, 303.

of an electromagnet. The heterogeneous pencil of particles, all of which follow the same course before entering the electric and magnetic fields, is split up into a number of groups of rays branching off in different directions. No two particles move along the same path unless they have the same masses and also the same velocities. It can be shown that all particles with the same masses but with different velocities move along the surface of a cone which is peculiar to the particular particle, so that if this cone is determined, the nature of the particle carrying the positive charge is also known; in this way, from a study of the path traversed by a particle, it is possible to

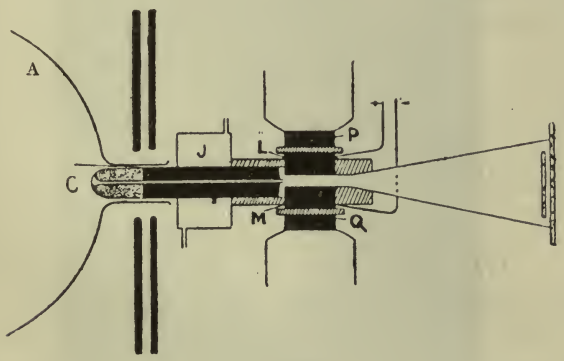


Fig. 203.

deduce its mass and therefore the chemical nature of the atom or molecule constituting the positive radiation. The cones are determined by observing their parabolic sections on a photographic plate placed in the path of the rays. A typical photograph obtained in this way is shown in Fig. 204. The photograph was obtained with the residues from liquid air containing the lighter gases; there are present lines corresponding to helium, neon, argon, and also a line of special interest corresponding to an atomic weight 22, which cannot be identified with the line of any known gas; for the possibility of it being due to molecules of CO_2 carrying a double charge of electricity is precluded by the fact that on passing the gases through tubes immersed in liquid air the line persisted, whereas the line at 44, due to carbon dioxide, disappeared. There seems to be no doubt that the line is due to a new gas of atomic weight 22 contained in the atmosphere and closely

associated in properties with neon; for it is found in all the specimens of neon which have been examined.

The method has resulted also in the highly interesting discovery of another element of atomic weight 3 derived from most solids when bombarded by cathode rays. It might be supposed that this gas was a polymeric modification of hydrogen with the formula H_3, but its properties are such as to render this supposition unlikely; for it is exceedingly stable, being

FIG. 204.

able to resist the action of oxygen and the action of prolonged electric discharge.

The nature of these positive rays is very complicated, since the particles constituting them may consist either of atoms or molecules with single or multiple charges; but there is no doubt that the phenomena afford a new and extremely delicate method of chemical analysis.

In 1896 Becquerel [1] found that uranium potassium sulphate crystals were able to affect a photographic plate wrapped up in black paper. The effect was produced also through thin glass or metal, and both by uranium metal itself and

[1] *Compt. rend.*, 1896, **122**, 188, 233, 386, 452.

by all its compounds, either in the solid state or in solution. The activity of a uranium salt enclosed in a thick lead box, and never exposed to light, was observed by Becquerel to continue undiminished for four years, and was not affected by variations of temperature from 200°C. to the temperature of liquid air. Becquerel also observed that the rays from uranium, which are known as the Becquerel rays, have the power of discharging an electroscope, whether positively or negatively charged. They are similar in these respects to the X-rays, but their action is feeble in comparison with that of the latter, since it requires several days' exposure to produce a marked action on a photographic plate with the Becquerel rays, whereas with the X-rays a photograph can be taken with an exposure of less than a minute.

Becquerel's discovery was followed in 1898 by the observation, made independently by Schmidt[1] and Mme. Curie,[2] that the compounds of thorium and minerals containing this element also emit radiations of a similar character to the Becquerel rays. These discoveries have led to the recognition of an entirely new class of substances which possess the remarkable property of radioactivity.

Radioactive substances spontaneously emit rays possessing in varying degrees the properties of canal, cathode, and X-rays. The phenomena available for the study of the radiations from such substances are:

(*a*) The action on the photographic plate.

(*b*) The phosphorescence produced in certain substances: *e.g.*, the platinocyanides, willemite (zinc silicate), kunzite, and Sidot's blende (crystalline zinc sulphide).

(*c*) The ionisation of gases produced by the rays.

The last of these lends itself most readily to quantitative measurements, and is generally employed for measuring the degree of radioactivity possessed by a substance.

According to the theory of the ionisation of gases of J. J. Thomson and Rutherford,[3] this effect is due to the production of "ions" or positively and negatively charged carriers in the gas, the rate of production being proportional to the intensity of the radiation. These ions move with uniform velocity through a uniform electric field, the positively charged towards the negative plate, and the negatively charged towards

[1] *Ann. Physik*, 1898, **65**, 141. [2] *Compt. rend.*, 1898, **126**, 1101.
[3] *Phil. Mag.*, [5], 1896, **42**, 392.

the positive plate, and their velocity is further proportional to the strength of the field. The separated ions also gradually recombine, the rate of recombination being proportional to the square of the number present. An ionised gas preserves its conducting power for some time after its removal from the presence of the ionising agent, and may be carried in a current of air so as to discharge an electroscope at some distance away.

The arrangement for measuring the rate of ionisation produced by X-rays or cathode rays or by the presence of radioactive material, is shown diagrammatically in Fig. 205.

The active material is placed at R on the lower of two insulated plates A and B, charged respectively negatively and positively by means of a battery connected to B and with the

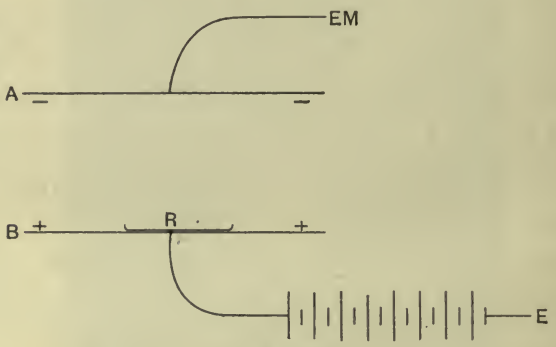


Fig. 205.

other pole earthed at E. The plate A is connected to one pair of quadrants of an electrometer E.M. of which the other pair of quadrants is earthed. The gas between the plates A and B being ionised at a constant rate, if no electric field be present, the number of ions soon reaches a maximum, when the rate of production of fresh ions is exactly compensated by the rate of recombination of the ions previously formed. If, however, B be kept charged to a constant potential V, the rate at which the plate A gains electric charge may be measured by the quadrant electrometer E.M. Positive ions travel to the negative plate A, and negative ions travel to the positive plate B, and there is thus a current through the gas which is measured by the rate at which A rises in potential.

When V is small the current is small, but as V increases the current rapidly rises to a limit, after which the current

remains constant even when the value of V is largely increased. This condition is not always attainable in practice, a slight increase of current generally occurring with increase of V. This limiting *saturation current* through the gas thus measures the charge carried by the ions produced per second by the radiation, that is, it is a measure of the radio-activity of the substance under examination. For uranium, and for substances not more than a thousand times as active as uranium, a difference of potential of about 300 volts is usually sufficient, but for radium, and for very active substances, the

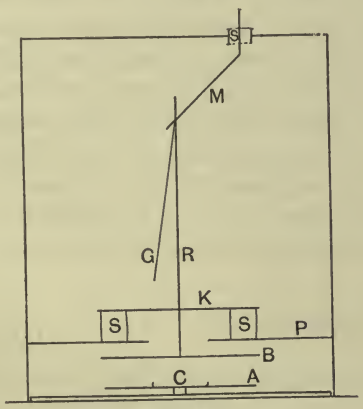


FIG. 206.

plates are placed close together, and a higher voltage may be necessary.

Frequently, some form of gold-leaf electroscope is used to measure the saturation current. Such an electroscope is shown in Fig. 206. A strip of gold-leaf G is attached to a vertical rod R, which is supported by the horizontal rod K, resting on two blocks of sulphur SS, by which the system is insulated. The rod R passes through an opening in the metal plate P, and terminates in a horizontal plate B, which is opposed to the removable plate A, on which the radio-active material C is placed. The whole is enclosed in a metal case and the motion of the gold-leaf is observed through an opening in the metal case, by means of a microscope of low power, provided with a micrometer eyepiece. M is a bent wire passing through an insulating plug of sulphur S in the top of the case; by means of this wire the electroscope can be charged. During an observation the metal case and the

lower plate A are connected to earth, and the time taken for the gold-leaf to pass over a fixed part of the scale is determined, this observation being corrected for the *natural leak* of the instrument, measured when no radioactive material is present. The measurements are generally comparative, uranium oxide being frequently employed as a standard of comparison. The instrument described above is typical of an electroscope used for radioactive measurements. The details of construction will of course depend upon the particular measurement to be made.[1]

In the examination of radioactive substances, and in the search for new radioactive material, the electroscope has proved an invaluable guide. Bunsen showed that 0·0000003 milligram of sodium could be detected by spectrum analysis; but for the detection of substances like radium the electroscope is many thousand times as sensitive as the method of spectrum analysis, for by its means a substance having only the ten-thousandth of the activity of uranium can be detected, whilst the activity of radium is about 2,000,000 times that of uranium.

Phenomena of Radioactivity.

651 The radiations from radium and most of the radioactive substances are found to be complex. The different kinds of radiation are distinguished by their different behaviour in a magnetic field and by their different power of penetrating metal screens, &c. By these methods it has been found that radium emits three different kinds of rays, which have been called by Rutherford α, β, and γ rays respectively.

The α rays are analogous to canal rays and are easily absorbed by thin metal foil and by a short column of air. Their deflection in a magnetic field is slight compared with that of the β rays, but is in the opposite direction, proving that they are positively charged. The magnitude of their deflection shows that they are moving with a velocity approximately one-tenth of that of light.

The β rays are identical with the cathode rays produced in a highly exhausted vacuum tube: they are deflected by a magnetic field in such a direction as to show that they are carriers of negative electricity. They are completely absorbed

[1] See Makower and Geiger, *Practical Measurements in Radioactivity* (Longmans, 1912).

by one millimetre of lead. Their velocity is, however, much greater than that of the cathode rays in a vacuum tube, the β rays from radium varying in velocity between about 10^{10} and nearly 3×10^{10} cm. per second. The penetrating power of the electrons increases rapidly with the velocity, and some of those expelled from radium penetrate a thickness of a millimetre of lead.

Besides the α and β rays, uranium, thorium, and radium compounds emit very penetrating rays known as the γ rays, whose penetrating power is 100 times that of the β rays, so that the rays can be detected after passing through several centimetres of lead. These rays are not deflected [1] in a magnetic field. They can easily be detected from a few milligrams of radium bromide enclosed in a lead vessel of 1 cm. thickness (which completely absorbs the α and β rays) by the luminosity they produce in a fluorescent screen of barium platinocyanide or of willemite, when observed in a dark room. The γ rays, which seem to be similar in nature to X rays, are usually associated with β rays, and are probably produced in some way from the β particles as they escape from the atom. It has, however, recently been shown by Chadwick [2] that γ rays may be produced in small quantity from α rays.

The different behaviour of the three kinds of ray in a magnetic field is diagrammatically illustrated [3] in Fig. 207.

R represents the radium compound placed at the bottom of a small cylindrical lead vessel, standing on a photographic plate AC. By a strong magnetic field applied at right angles to the plane of the paper and directed towards the paper, the three types of radiation are separated: the γ rays take a straight course without being affected by the magnetic field, the β rays are deflected to the right, describing circular paths, and affect the photographic plate on the right of R, while the α rays are slightly deflected to the left, but are quickly absorbed by the air.

The phosphorescence produced in a zinc sulphide screen by radium is chiefly due to the α rays. This phenomenon was discovered by Crookes,[4] and is well exhibited by his apparatus, known as the *spinthariscope*. In this a fine metallic point,

[1] Villard, *Compt. rend.*, 1900, **130**, 1010, 1178; Becquerel, *ibid.*, 1154.
[2] *Phil. Mag.*, 1913, [6], **25**, 193.
[3] Rutherford, *Radioactive Substances*, p. 116.
[4] *Proc. Roy. Soc.*, 1903, A., **71**, 405.

which has been dipped in a solution of a radium salt, is fixed a millimetre or two above a zinc sulphide screen, which is examined with a magnifying glass in darkness. The surface of the screen is then seen to be dotted with flashes of light, which follow each other rapidly, and this action is kept up without any apparent diminution for years. It has been shown that nearly every α particle striking the screen produces a flash of light, and this property has been employed to count the number of α particles emitted by a source of radiation.[1]

The velocity of the α rays is not easy to determine exactly,

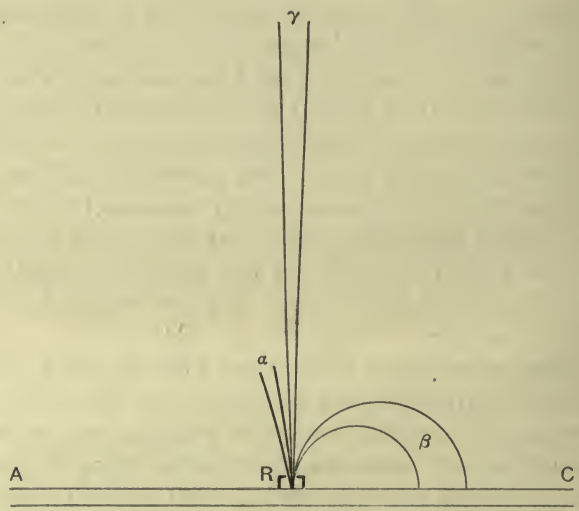


FIG. 207.

because of the smallness of the deflection of the α particles in an electric or magnetic field. Rutherford[2] has found it to be $2{\cdot}06 \times 10^9$ cm. per second, whilst the ratio $e/m = 5{\cdot}07 \times 10^3$. This value of e/m is almost exactly half that of the hydrogen ion in electrolysis.

The velocity of the α particle emitted from different substances varies, and the foregoing figure applies to that given off by the substance known as radium C (p. 1437). On the other hand, the ratio e/m is constant. When the velocity of the α particle falls below a certain limit, which is about 40 per cent.

[1] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, A., **81**, 141, and Regener, *Verh. deut. physikal. Ges.*, 1908, **19**, 78, 351.

[2] *Phil. Mag.*, 1906, [6], **12**, 348.

of the velocity given above, the particle ceases to produce the effects characteristic of radioactivity, and passes beyond the reach of our present experimental methods. When the velocity of an α particle has thus been reduced, the particle seems to be brought to rest within a very short distance, so that the α particle appears to be suddenly stopped after traversing a certain thickness of matter. The maximum distance which an α particle can penetrate through air at normal temperature and pressure has been called by Bragg the *range* of the α particle. The ionisation produced by an α particle near the end of its range increases very rapidly and then suddenly vanishes. The range of different α particles varies from 2·37 cm. to 8·15 cm. and is characteristic of the particular product from which the α particle is emitted. A relation has been obtained by Geiger and Nuttall[1] between the range and the rate of decay of radioactive products. The nature of an α particle has been the subject of much speculation and many considerations point to its identity with an atom of helium. Now the value of e/m for a helium atom of atomic weight 4 carrying the same ionic charge as a hydrogen ion in electrolysis, should be $2{\cdot}5 \times 10^3$, and we have seen that the value of e/m for an α particle is almost exactly twice that number. Now it has been shown by Rutherford and Geiger[2] that an α particle is associated with twice the atomic charge, whence it follows that the atomic weight of the α particle is 4, *i.e.* that the α particle is a charged atom of helium. This has been confirmed by direct experiment by Rutherford and Royds (p. 1433).

Associated with the expulsion of α particles is the phenomenon of radioactive recoil. When an α particle of mass m is emitted by an atom of mass M the residual atom, the mass of which must be $M-m$, will be projected in a direction opposite to that in which the α particle is travelling with a velocity V given by the equation $(M-m)V=mv$, where v is the velocity of the α particle. Now since the velocity of an α particle is about 2×10^9 cm./sec., and since its atomic weight is 4 and that of a radioactive atom about 200, it follows, from the above equation, that the velocity with which the residual atom must recoil must be 4×10^7 cm. per second. This atom which constitutes the next product (p. 1424) in the disintegration series to the product from which the α particle is emitted, will

[1] *Phil. Mag.*, 1911, **22**, 613. [2] *Proc. Roy. Soc.*, 1908, A, **81**, 162.

travel a considerable distance if free to move through a vacuum, as has been shown by Russ and Makower.[1] The recoiling atom is positively charged and can be deflected in electric and magnetic fields and this property can be used, as in the case of α rays, to determine the velocity of projection and the value of e/m for the recoiling atoms. The employment of this method promises to afford a means of determining the atomic weights of several radioactive substances. When projected into air at atmospheric pressure, a recoil stream does not penetrate more than about a tenth of a millimetre; but the recoiling atoms after being stopped still retain their positive charges and can thus be collected on the negative electrode in an electric field. By this process many radioactive products have been separated.[2] Although an atom when it recoils possesses only $\frac{1}{50}$ the energy of the α particle it is able to produce ionisation in gases, as has been shown by Wertenstein.[3]

When the β particles are expelled and carry with them negative electricity they must leave the radium positively charged. This is clearly shown by the contrivance called the *Radium clock*.[4] This consists of a small tube containing some radium compound, which is attached at its upper end by an insulating rod of quartz to the top of a wider tube within which it hangs. At the lower end of the small tube two thin gold leaves are attached, the outer surface of the tube having been coated with phosphoric acid to render it conducting. The larger tube is coated on the inside with tinfoil, connected to earth, and is exhausted as completely as possible to reduce the loss of charge consequent on ionisation of its gaseous contents. With 30 mgrs. of pure radium bromide the leaves are observed to diverge, until they touch a piece of metal connected to earth, when they collapse, and then gradually diverge again, this periodic movement of the leaves occupying about a minute. The effect is due to the stoppage of the α particles with their positive charge by the thin glass of the inner tube, which, however, allows the β particles to pass through. The rhythmic motion continues with regularity for years, and it is estimated that it would take more than a thousand years for the emission of β particles to fall to half its present rate, when the movement of the gold leaves would take place in two minutes instead of one.

[1] *Proc. Roy. Soc.*, 1909, A., **82**, 205.
[2] Hahn, *Verh. deut. physikal. Ges.*, 1909, **11**, 55.
[3] *Le Radium*, 1912, **9**, 6. [4] Strutt, *Phil. Mag.*, 1903, [6], **6**, 588.

FIG. 208.—α rays from radium. Some of the α particles have traversed the air before the expansion, others after the expansion.

The emission of β rays from radioactive atoms is far more complicated than the emission of α rays; for although, as in the case of α rays, it seems possible that only one β particle is emitted for each atom disintegrating,[1] the particles are emitted with very different velocities. By subjecting the radiation to a magnetic field the rays can be separated into definite groups known as a *magnetic spectrum*. It has been shown that in the case of radium and its disintegration products, there are a great number of groups of rays.[2] It seems probable that the β particles from any particular product are all projected with the same initial velocity, but that they are retarded to different extents while escaping from the atom.[3]

The phenomena involved in the passage of α, β, and γ rays through air have been very strikingly demonstrated by C. T. R. Wilson.[4] When an α or β particle passes through air, very intense ionisation is produced in the track of the particle. If

FIG. 209.—A complete α ray from radium emanation.

[1] Moseley, *Proc. Roy. Soc.*, 1912, A., **87**, 230.
[2] Danysz, *Le Radium*, 1913, **10**, 5.
[3] Rutherford, *Phil. Mag.*, 1912, [6], **24**, 453.
[4] *Proc. Roy. Soc.*, A., 1912, **87**, 277.

the air is saturated with water vapour, and if, by sudden expansion, the air is cooled immediately after the passage of the particle, a cloud is formed along its track. By a suitable timing device, an instantaneous photograph is obtained of the cloud, which thus renders visible the track of the particle. In the case of the α particle the track is almost straight, showing only an occasional and sudden deflection or "scattering" from its course. At the end of its range, the scattering of the α particle is more marked (Fig. 208). The photographs exhibit also the ionisation produced by the residual atom recoiling

FIG. 210.—β rays produced by γ radiation.

from the α particle (Fig. 209). In the case of the β particle, the path is much more tortuous, showing the greater part played by scattering in the case of these particles (Fig. 210). With X rays the photographs are much more complicated and consist of innumerable ramifications along the path of the rays. The photographs are such as to indicate that the ionisation is not produced by the X rays themselves, but by secondary β rays produced in their path—a suggestion first put forward by Bragg (Fig. 211).[1]

A remarkable property of the compounds of radium, first

[1] *Phil. Mag.*, 1910, **20**, 385; *Proc. Roy. Soc.*, 1911, A., **85**, 349.

observed by Curie and Laborde,[1] is that of maintaining themselves constantly at a higher temperature than the surrounding atmosphere, the difference observed being from 3° to 5°. The continuous emission of heat which this shows was found by Curie and Dewar to be unaffected at the temperature of liquid air or liquid hydrogen. They found that 0·7 grm. of pure radium bromide, surrounded by liquid hydrogen, caused the volatilisation of 73 c.c. of hydrogen per minute. From data thus obtained it appears that one gram of radium emits as much energy as would decompose one gram of water every day, or, otherwise expressed, it appears that one pound of radium emits energy at the rate of 10,000 horse-power.

ERRATUM

P. 1423, line 17, *for* "10,000 horse-power," *read* "nearly one-tenth horse-power."

system flies off with the velocity it had in the atom.

The view that the energy emitted by radioactive bodies is derived from a store in the atoms is supported by the fact that the energy is given off at a rate which is quite unaffected by variations in physical and chemical conditions such as temperature, pressure, or mode of combination of the element; for it is difficult to account for these facts on any other supposition.

Fig. 211.—Ionisation by X ray beam about 5 mm. in diameter.

The physical nature of the α rays is now well understood; but our knowledge of the β and γ radiations is still imperfect and is constantly being added to or modified.

[1] *Compt. rend.*, 1903, **136**, 673.

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Fig. 211.—Ionisation by X ray beam about 5 mm. in diameter.

It does not appear probable that radium derives its enormous store of energy from external sources. The more probable supposition is that the α particles are originally in rapid motion in the atom and that an α particle when released from the atomic system flies off with the velocity it had in the atom.

The view that the energy emitted by radioactive bodies is derived from a store in the atoms is supported by the fact that the energy is given off at a rate which is quite unaffected by variations in physical and chemical conditions such as temperature, pressure, or mode of combination of the element; for it is difficult to account for these facts on any other supposition.

The physical nature of the α rays is now well understood; but our knowledge of the β and γ radiations is still imperfect and is constantly being added to or modified.

[1] *Compt. rend.*, 1903, **136**, 673.

The Products of Radioactive Change.

652 A most remarkable property possessed by radium, actinium, and thorium, but not by uranium, is the power of giving off continuously a radioactive gas which can be condensed by extreme cold. The radioactivity of thorium was observed to vary capriciously, and this inconstancy was traced by Owens [1] to currents of air which removed the gas. Rutherford [2] gave the name of *emanation* to this remarkable gas, which discharges an electroscope, affects a photographic plate, diffuses through porous substances, and can be washed through water without loss of activity; it is condensed at the temperature of liquid air,[3] but not at that of solid carbon dioxide. It thus behaves differently from the ionised gas produced by X rays, since the conductivity of such ionised gas is completely removed by passing through cotton wool, or by bubbling through water. The emanation from thorium rapidly loses its activity with time, falling to half value in about one minute.[4] Dorn [5] showed that radium compounds also give off an active emanation, the amount obtained being much increased by heating the compound or by dissolving it in water.

These discoveries have led to the recognition of a hitherto unsuspected phenomenon, the spontaneous disintegration of the atoms of an element in a series of stages, each stage being marked by the emission of certain definite particles and the production of a substance of lower atomic weight, characterised by definite physical and chemical properties. According to this *theory of the spontaneous disintegration of matter*, put forward by Rutherford and Soddy, in each second a small proportion of the atoms of a radioactive material becomes unstable; these atoms break up with explosive violence, the change being accompanied by the expulsion of an α or a β particle. The atom is probably a complex aggregate of known or unknown forms of matter, which breaks up spontaneously with an evolution of energy enormous compared with that released in ordinary chemical action. These aggregates behave like atoms,

[1] *Phil. Mag.*, 1899 [5], **48**, 360. [2] *Phil. Mag.*, 1900 [5], **49**, 1.

[3] Rutherford and Soddy, *Phil. Mag.*, 1903, [6], **5**, 561.

[4] le Rossignol and Gimingham (*Phil. Mag.*, 1904, [6], **8**, 107) found that the activity fell to half value in fifty-one seconds; Bronson (*Amer. J. Sci.*, 1905, **19**, 185) found fifty-four seconds.

[5] *Naturforsch. Ges. Halle*, (1900).

and cannot be split up by ordinary chemical or physical agencies.

The rate of change of any single product at any time is found to be proportional to the number of atoms present at that time, so that the change follows the same law as a monomolecular chemical reaction. Hence if N_0 represents the number of atoms of a radioactive substance present at any time, and N the number present after the lapse of time t, then:

$$N = N_0 e^{-\lambda t},$$

where λ is known as the *disintegration constant* of the substance, and e is the base of the natural logarithms. By differentiating this equation it can easily be seen that:

$$\frac{dN}{dt} = -\lambda N,$$

from which it follows that λ represents the fraction of the total number of atoms undergoing disintegration at any instant. The rate of disintegration of a substance is expressed by the constant λ; but it is more usual to define the rate of decay by the time T taken for half the number of atoms present to disintegrate. The value of T i obviously connected with that of λ by the relation,

$$T = \frac{1}{\lambda}\log_e 2 = \frac{0{\cdot}693}{\lambda}.$$

The quantity T is known as the *half value period* of the substance.

When an active product is removed from a radioactive substance, *e.g.* the emanation from a thorium compound, the activity of the isolated product gradually falls, according to the foregoing law, whilst that of the parent substance rises, also according to that law, owing to the accumulation of a fresh quantity of the active product. After the expiration of any period it is found that the isolated product has lost a certain fraction of its original activity whilst the parent substance has regained the same fraction of the activity which it had lost.

The determination of the exact series of changes undergone by a radioactive substance is a matter of considerable difficulty, and the solution of the problem is due to the brilliant researches of Rutherford and his colleagues. For this purpose it is necessary to measure separately the radioactivity due to the α, the β, and the γ rays, and to construct curves showing the

variation of each of these with time. The differentiation of the action of the three types of ray is effected by taking advantage of their different penetrating powers, sheets of metal of sufficient thickness to absorb the α rays, or both the α and β rays, being interposed between the material and the electroscope. The β and γ rays are also often separated by deflecting the β rays by a magnetic field.

From a comparison of the curves thus produced the number of changes which occur, the nature of the radiation, and the rate of the change can be deduced. The matter is much simplified when the products can be separated either physically or chemically from the parent substance and subjected to examination, as is the case with the emanation of radium, &c. In a few cases it is necessary to assume that changes occur unaccompanied by any measurable radiation, and these are described as rayless, although it is probable that rays which escape our methods of measurement are in reality emitted.

In most cases of radioactive changes, the products are formed from each other in a direct series of transformations. Thus any particular type of radioactive matter breaks up at a perfectly definite rate always giving rise to the same substance —the next member in the radioactive series. Some very interesting cases have, however, recently come to light in which it appears that certain types of atom can break up in two different ways, thus giving rise to two distinct products. This has been found to be the case with radium C[1] (p. 1437) and thorium C[2] (p. 1441). Thus radium C usually disintegrates with the production of radium D, but occasionally an atom of radium C gives rise to a new product, radium C_2, instead of radium D.[3] In the case of thorium C the proportion of atoms giving rise to a branch product is much greater; for one-third of the atoms of thorium C break up with the emission of α rays and produce thorium D, whereas two-thirds emit β rays and give rise to the product thorium C_2.[4]

Recently great interest has centred in the question of the position of the radioactive elements in Mendeléeff's periodic system. It has been pointed out by Fajans[5] that when a transformation takes place with the emission of a β particle

[1] Hahn and Meitner, *Physikal. Zeit.*, 1909, **10**, 697.
[2] Hahn and Meitner, *Verh. deut. physikal. Ges.*, 1909, **11**, 55.
[3] Fajans, *Physikal. Zeit.*, 1911, **12**, 369.
[4] Marsden and Darwin, *Proc. Roy. Soc.*, 1912, A., **87**, 17.
[5] *Physikal. Zeit.*, 1913, **14**, 131.

the resulting product is more electronegative than the parent substance. Exactly the reverse is the case when a transformation takes place with the emission of an α particle. It has been shown by Soddy [1] that during an α ray transformation the atom passes from a family of even number in the periodic table to the next lower even family, the families of the odd numbers being always missed. This rule has been generalised and extended to the case of β ray transformations by Russell,[2] and by Fajans,[3] who has shown that in all cases in which the chemical nature of the radioactive products is sufficiently well known to test its correctness, the following rule holds: In an α ray transformation the product generated falls into a group *two* places lower than that to which the parent substances belongs. On the other hand, in a β ray transformation the product generated falls into a group *one* place higher than that of the parent substance. These laws are exemplified in the table (p. 1429). It will be seen that it is necessary to assume the existence of a few undiscovered products; but there is independent evidence which makes their existence probable. Further, it will be seen that a single space in the periodic table is in each case occupied by several different products which are chemically more alike than any pair of non-radioactive elements, for they are inseparable by any chemical process and can be distinguished only by their radioactive properties. Thus for instance Actinium X, Thorium X, Radium, and Mesothorium are inseparable by any chemical process.

RADIUM. Ra = 226·4.

653 The mineral pitchblende—an impure oxide of uranium (p. 1105)—is the richest source of radioactive substances. Whilst investigating this material Mme. Curie found that some specimens of pitchblende had four times the activity of the metal uranium, and by chemical methods M. and Mme. Curie succeeded in separating two new substances, characterised by intense radioactivity, which they named polonium and radium.

The history of Mme. Curie's successful search for radioactive

[1] "Chemistry of the Radio-Elements," p. 30.
[2] *Chem. News*, 1913, **107**, 49.
[3] *Ber.*, 1913, **46**, 422, and *Physikal. Zeit.*, 1913, **14**, 136.

substance in the residues of the pitchblende of Joachimsthal is of great interest.[1]

For the extraction of uranium the crushed ore is roasted with sodium carbonate, and washed with warm water and dilute sulphuric acid; the solution contains the uranium, and the insoluble residues are rejected. The Austrian Government presented Mme. Curie with a ton of these residues, the activity of which was found to be about four and a half times that of uranium. The residues consist chiefly of the sulphates of lead, barium, and calcium, silica, alumina, and oxide of iron, and contain also small amounts of copper, bismuth, zinc, cobalt, manganese, nickel, vanadium, antimony, thallium, the rare earths, columbium, tantalum, arsenic, &c. The search for the radioactive substances which cause the high activity of pitchblende was made in the early stages by the ordinary methods of chemical analysis. The residues were first treated with boiling soda, and the sodium sulphate formed removed by washing, together with lead, strontium, and aluminium. The insoluble portion was attacked by hydrochloric acid, which dissolves most of it. The residue from this operation was found to contain a radioactive substance which received the name *radium*. The solution also was found to contain radioactive substances, one of which is precipitated by sulphuretted hydrogen together with bismuth, and received the name *polonium*. A second, discovered by Debierne,[2] and named *actinium*, is contained in the hydroxide precipitated by ammonia in the filtrate from the precipitated sulphides.

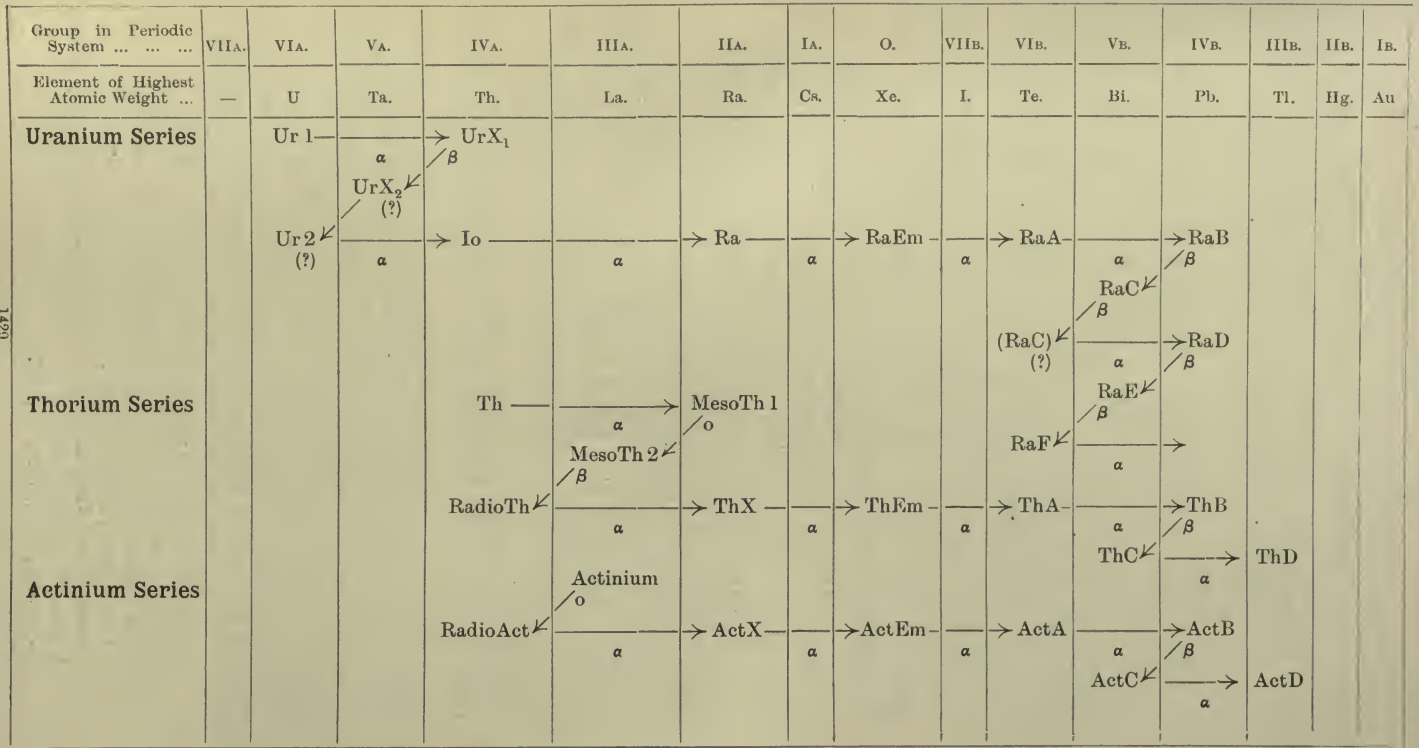
654 *Purification and Properties of Radium Salts.*—The radium is extracted from the insoluble portion mentioned above by boiling with a strong solution of sodium carbonate, which transforms the barium and radium into carbonates. These are washed and dissolved in hydrochloric acid, and sulphuric acid is added, which precipitates the sulphates of barium and radium, with calcium, lead, iron, and a trace of actinium.

One ton of the Joachimsthal residues yielded from 10 to 20 kilos. of the crude sulphates, of an activity about 60 times that of uranium. The crude sulphate is next transformed into chloride, treated with sulphuretted hydrogen, the filtrate oxidised with chlorine, and precipitated with

[1] See translation of thesis presented to the Faculté des Sciences of Paris, *Chem. News*, 1903, **88**, 85.

[2] *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 906; 1903, **136**, 446, 767.

A Periodic Arrangement of the Radio-Elements.



ammonia. The filtrate is then precipitated with sodium carbonate, and the carbonates converted into chlorides, and washed with pure strong hydrochloric acid, which dissolves calcium sulphate and leaves the chlorides of barium and radium.

These chlorides are then separated by repeated fractional crystallisation from water. When only a small quantity of crystals is allowed to separate, it is found that five times as much radium separates with the crystals as is left in solution. By repeating this process a great number of times a fraction of a gram of radium chloride was obtained of an activity a million times that of uranium.

Giesel [1] employs the bromides instead of chlorides in the fractional separation of radium and barium: the radium separates with the least soluble portion, and about eight fractionations effect the removal of most of the barium.

The compounds of radium resemble those of barium in properties. The crystals of the chlorides are isomorphous with those of barium chloride; when pure they are colourless, but those containing both barium and radium become coloured yellow, orange, or pink. The solution in water evolves hydrogen and oxygen continuously. The *nitrate*, *carbonate*, *sulphate*, *bromide*, and *platinocyanide* resemble the corresponding salts of barium very closely. When freshly prepared the anhydrous bromide exhibits a splendid blue phosphorescence, which gradually disappears, but is more permanent in the presence of barium salts.

Radium has been prepared in the metallic state by Curie and Debierne.[2]

655 *Spectrum of Radium.*—Radium is found to have its own characteristic spectrum and this affords one of the strongest proofs of its elementary character. Radium bromide colours the Bunsen flame a pure carmine-red, and the flame shows four bands or lines in the red and a strong line in the blue.

The spectrum [3] of radium has been investigated by Demarcay,[4] Runge,[5] Exner and Haschek,[6] Runge and Precht,[7] and Crookes.[8]

[1] *Ann. Phys. Chem.*, 1899, [2], **69**, 91; *Ber.*, 1902, **35**, 3608.
[2] *Compt. rend.*, 1910, **151**, 523; *Le Radium*, 1910, **7**, 309.
[3] See Watts, *Index of Spectra*, Appendix O, p. 40.
[4] *Compt. rend.*, 1898, **127**, 1218.
[5] *Ann. Physik*, 1903, **12**, 407.
[6] *Wien. Ber.*, 1901, July 4.
[7] *Ann. Physik*, 1904, **14**, 418.
[8] *Proc. Roy. Soc.*, 1904, **72**, 295.

The most intense lines in the spark spectrum are 4683, 4436, 4341, 3814, 3650, 2814, and 2709.

656 *Atomic Weight of Radium.*—The atomic weight was determined by estimating the percentage of chlorine in the anhydrous chloride. As only about one decigram of substance was available, Mme. Curie [1] made preliminary determinations of the atomic weight of barium with about the same weight of pure barium chloride, and found that good results could be obtained. With barium chloride of an activity 600 times that of uranium the number 137 was obtained, with that of 7,500, the result was 143·8, and with chloride of increasing activity the atomic weight increased giving about 225 with a specimen which only showed very faint traces of the brightest barium lines in the spectroscope. This sample was repurified, and gave the following results:

Radium chloride taken.	Silver chloride obtained.	Atomic weight (H = 1).
0·09192	0·08890	225·7
0·08936	0·08627	226·2
0·08839	0·08589	224·5

The activity of this chloride was about two million times that of uranium. A later determination made by Mme. Curie in 1907 gave the value 226·4,[2] and Thorpe [3] found the value 226·7. Ramsay and Gray [4] give the value 226·45. A determination with a large quantity of radium, which therefore probably gives the most reliable result, has been made by Hönigschmid,[5] who finds the atomic weight to be 225·95. This number is in harmony with the chemical behaviour of radium, which then finds its place in the periodic table in Group II, Series 12.

Runge and Precht [6] have made calculations of the atomic weight of radium from the spectrum, and have deduced the value 256·3. This assumes that radium really belongs to the group of alkaline earths, and is based upon the observation that radium, like Mg, Ca, Sr, and Ba, has in its spectrum pairs of lines, repeated several times, with a constant difference of oscillation frequency, and that the distance apart of these

[1] *Compt. rend.*, 1899, **129**, 760; 1900, **131**, 382; 1902, **135**, 161.
[2] *Compt. rend.*, 1907, **145**, 422.
[3] Thorpe, *Proc. Roy. Soc.*, 1908, A, **80**, 298.
[4] *Proc. Roy. Soc.*, 1912, A, **86**, 270.
[5] *Sitzungsber. K. Akad. Wiss. Wien*, 1911, IIa, **120**, 1617.
[6] *Phil. Mag.*, 1903, [6], **5**, 476.

pairs for the different elements, increases in a regular manner with the atomic weight (see p. 157).

It must be remembered that this calculation amounts to an *extra*polation passing over the unknown element below barium in the periodic table (Series 10), so that we are extrapolating for a considerable distance. It has been pointed out [1] that the result of the calculation is probably too high, for the reason that a similar calculation of the atomic weight of mercury from those of zinc and cadmium gives the atomic weight too high by about 22 units: it seems probable that this method has a tendency to give results too high for the higher atomic weights. A similar criticism has been made by Rudorf.[2] Furthermore in the case of radium the atomic weight obtained by the spectroscopic method disagrees with strong evidence derived from a consideration of the disintegration theory (p. 1424); for there is reason to believe that radium is formed from uranium with the emission of three α particles. Taking the atomic weight of uranium as 238·5 the atomic weight of radium should be 226·5, a value which agrees with the values found by the chemical method.

The question of establishing a standard quantity of radium was discussed at the International Congress of Radiology (Brussels, 1910). As a result 21·99 milligrams of the radium chloride used by Mme. Curie in the determination of the atomic weight of radium have been sealed in a small glass tube and deposited at Paris in the Bureau International des Poids et Mesures. A similar reserve standard has been deposited in Vienna. With the aid of these standards the quantity of radium in any sample can be estimated by comparing the γ radiation it emits with that emitted by the standard.

Products formed from Radium by Radioactive Change.

657 *Production of Helium by the Spontaneous Change of Radium.*—In 1903 Ramsay and Soddy [3] made the remarkable discovery that helium is given off by radium. They found that 30 milligrams of pure radium bromide (which had been prepared three months) when dissolved in water liberated gases amongst which were hydrogen and oxygen. These were removed

[1] Watts, *Phil. Mag.*, 1903, [6], **6**, 64.
[2] *Zeit. physikal. Chem.*, 1904, **50**, 100.
[3] *Proc. Roy. Soc.*, 1903, **72**, 206; 1904, **73**, 346.

by passing the gas over a red-hot spiral of partially oxidised copper wire, and then over phosphoric anhydride into a vacuum tube joined on to a small U-tube.

By placing the U-tube in liquid air most of the emanation present was condensed. The spectrum of the gas left in the vacuum tube, including the carbon dioxide present in the original gas, was then observed and showed the characteristic helium line D_3. In a repetition of the experiment the helium lines at 6677, 5876, 5016, 4922, 4713 and 4472 were observed, as well as three unknown lines at 6180, 5695, and 5455. They also found that the emanation alone yielded helium in about three days.

These observations have been repeated and confirmed by Dewar and Curie [1] and by Himstedt and Meyer.[2] The latter observers sealed up 30 milligrams of radium bromide in an exhausted vacuum tube. The tube showed the lines of hydrogen and an oxide of carbon at first, but after four months the helium lines appeared.

Before the discovery of the production of helium in radioactive processes it was suggested by Rutherford and Soddy [3] that this gas might be a disintegration product of the radio-elements. This has since been proved by Rutherford and Royds [4] by sealing up some radium emanations in a glass tube, the thickness of the walls of which was only 0·01 millimetre. The *a* particles which passed through the walls of this tube were collected in a vessel which surrounded it; after some days the spectrum of helium could be detected in the outer vessel, proving that the *a* rays consisted of charged atoms of helium.

The rate of production of helium from radium has been measured by Dewar,[5] and by Boltwood and Rutherford.[6] For one gram of radium (metallic) in equilibrium with the emanation, radium A, and radium C, the latter find that 156 cubic millimetres of helium are produced per year. Dewar found the value 169 cubic millimetres per year, which must, however, be slightly corrected to be comparable with the number found by Boltwood and Rutherford on account of the difference in the values of the radium standards used in the two sets of experiments When thus corrected the value found by Dewar becomes

[1] *Compt. rend.*, 1904, **138**, 190. [2] *Ann. Physik*, 1904, **15**, 184.
[3] *Phil. Mag.*, 1902, **4**, 569; 1903, **5**, 576.
[4] *Phil. Mag.*, 1909, **17**, 281.
[5] *Proc. Roy. Soc.*, 1908, A., **81**, 280; 1910, **83**, 404.
[6] *Phil. Mag.*, 1911, **22**, 586.

164 cubic millimetres. The volume of helium to be expected from theoretical considerations is 158 cubic millimetres per gram of radium per year.

658 *Radium Emanation.* — The emanation is continuously produced from radium compounds and is itself strongly radioactive. A portion of it escapes, but the remainder is occluded in the compound, adding its radiation to that of the radium compound. To this is due the phenomenon, observed by Curie, that the activity and emission of heat of radium compounds vary with their age, the activity increasing for about a month after preparation, when it becomes steady. This state of radioactive equilibrium is reached when the rate of production of fresh emanation balances the rate of change of that already formed.

The emanation is formed from radium by the expulsion of an α particle and itself passes into the next lower product by a similar change. The period of half transformation for radium is about 2,000 years, and for the emanation 3·85 days. By collecting and measuring the emanation from 0·06 gram of radium bromide, Ramsay and Soddy conclude that the maximum amount of emanation to be obtained from one gram of radium is one cubic millimetre. This quantity is known as one *curie.* Later determinations by Rutherford,[1] Debierne,[2] and Gray and Ramsay[3] give the volume of one curie of emanation as 0·6 cubic millimetre.

The emanation is most readily obtained by dissolving the radium compound in water and removing the gases produced. This is best done by causing the solution to boil under reduced pressure. If air be passed through a radium solution large quantities of a mixture of air with the emanation may be obtained, and this may be stored in a gas-holder, and the electrical and photographic action examined for days after its production. The emanation can also be removed by heating the salt. When mixed with a large volume of air it condenses at $-154°$; but it must be remembered that in these circumstances the partial pressure of the emanation is exceedingly minute. When purified and at atmospheric pressure the emanation boils at $-65°$.[4] When at very low partial pressures, the condensation point of the emanation seems to depend upon the nature of the surface

[1] *Phil. Mag.*, 1908, **16**, 300. [2] *Compt. rend.*, 1909, **148**, 1264.
[3] *Journ. Chem. Soc.*, 1909, **95**, 1073.
[4] Rutherford, *Phil. Mag.*, 1909, **17**, 723.

upon which it condenses.[1] If the emanation obtained from a few milligrams of radium bromide by heating a solution be condensed in a small U-tube surrounded by liquid air, the U-tube being connected with a larger tube containing a small phosphorescent screen of zinc sulphide, and the whole apparatus connected with an air-pump, the behaviour of the emanation can be watched by means of the phosphorescence of the screen. The apparatus being partially exhausted, and the U-tube immersed in liquid air, no luminosity of the screen is observed, but if the liquid air be removed, in a few minutes the emanation diffuses into the wider tube, and the screen becomes brightly phosphorescent. If the U-tube be re-immersed in liquid air the emanation re-condenses, but the phosphorescence of the screen dies away only slowly, being maintained for some time by the production of an active deposit on the glass.

In another experiment a quantity of the emanation was collected in a small glass tube, which was seen to phosphoresce brightly under the rays from the emanation, and in a dark room the passage of the emanation from point to point of the tube could be traced. On opening the tap which connected the tube with the pump the slow flow of the emanation through the capillary portion of the tube and its more rapid passage through the wider portions was well seen.

The emanation obeys Boyle's law. Attempts to determine its density by measuring its rate of diffusion show that it is a heavy gas, of a density about 100; the method of diffusion is, however, for a variety of reasons unsuitable for determining the atomic weight of the emanation. From a consideration of the disintegration theory of radioactive changes, the atomic weight of radium emanation should be 222·4. Assuming the emanation to be monatomic, Gray and Ramsay[2] find the value 223, by a direct determination of its density with a specially constructed sensitive balance. The emanation belongs to the helium-argon group of gases, and like them resists attack by all chemical agents that have been tried. It is not affected when led in tubes over platinum black, copper oxide, zinc dust, &c., at a high temperature, and is unaffected by prolonged sparking with oxygen over caustic potash.

The spectrum of the emanation was first examined by

[1] Laborde, *Le Radium*, 1909, **6**, 289; 1910, **7**, 294; Boyle, *Phil. Mag.*, 1910, **20**, 955.

[2] *Proc. Roy. Soc.*, 1911, **A**, **84**, 536.

Ramsay and Collie,[1] and later by Rutherford and Royds,[2] Cameron and Ramsay,[3] Watson,[4] and Royds.[5] The brightest lines are those of wave-lengths: 4681·1, 4644·7, 4460·0, 4350·3, 4308·3, 4203·7, 4166·6, 4018·0, 3982·0, 3753·6, 3664·6.

Rutherford and Barnes[6] have made experiments on the heat emission by radium bromide and by the emanation obtained from it. The heat emission per gram of radium bromide was found to be 65 gram-calories per hour (which corresponds to 110 gram-calories per hour per gram of radium itself). The emanation was then driven off, and condensed by means of liquid air. After removal of the emanation the heat emission of the radium bromide fell off in three hours to about one quarter (27%), and then slowly increased, reaching its original rate in about a month. The heat emission from the separated emanation rose to a maximum in three hours, and then slowly decayed, falling to half value in about 3·7 days. The rate of decay of the emanation and the rate of recovery of the radium compound are both expressed by the exponential formula:

$$Q_t = Q\epsilon^{-\lambda t},$$

where Q is the heat emission at first, and Q_t that after a time t, λ being the constant of change. The radioactivity itself also follows a similar law, but the variation in the heat emission both of radium itself and of the emanation correspond approximately to the activity as measured by the α rays and not to that of the β or γ rays. The heat emission of radium is thus seen to correspond approximately with the expulsion of α particles.

The most recent and accurate determinations of the heating effect of radium are by Meyer and Hess,[7] and by Rutherford and Robinson.[8] The former give, for the heat emitted by one gram of radium in equilibrium with its disintegration products, the value 132·3 and the latter the value 135 gram-calories per hour. Rutherford and Robinson have also determined the heat emitted by each of the disintegration products separately, and also estimate that the β rays contribute 3·5 per cent., and the γ rays 5·2 per cent. of the total heating effect of

[1] *Proc. Roy. Soc.*, 1904, **73**, 470.
[2] *Phil. Mag.*, 1908, **16**, 313.
[3] *Proc. Roy. Soc.*, 1908, A, **81**, 210.
[4] *Proc. Roy. Soc.*, A, 1909, **83**, 50.
[5] *Phil. Mag.*, 1909, **17**, 202.
[6] *Phil. Mag.*, 1904, [6], **7**, 202.
[7] *Wien. Ber.*, 1912, **121**, 603.
[8] *Phil. Mag.*, 1913, **25**, 312.

radium. The observed heat emission is in good agreement with the calculated kinetic energy of the radiations. The heat emitted by radium and its products of disintegration is shown in the following table.

	Heating effect in gram calorics per hour, corresponding to one gram of radium.			
	α rays.	β rays.	γ rays.	Total.
Radium	25·1	—	—	25·1
Emanation	28·6	—	—	28·6
Radium A	30·5	—	—	30·5
Radium B } Radium C }	39·4	4·7	6·4	50·5
Totals	123·6	4·7	6·4	134·7

When the emanation is left in contact with water, the latter is decomposed, a mixture of hydrogen and oxygen containing an excess of hydrogen being evolved. About 0·03 cmm. of emanation yielded 2—4 c.c. of gas in different experiments, containing 3—14 per cent. of hydrogen in excess. The origin of this excess is not at present understood,[1] but it is probably in some way connected with the formation of ozone. The emanation is also capable of bringing about the slow combination of gaseous hydrogen and oxygen.

As already mentioned, the emanation on preservation yields helium, the volume of the latter being about 3·5 times as great as that of the emanation.[2]

659 *Radium A, B, C, D,* and *E.* — The radium emanation induces radioactivity on the glass in which it is contained; on removing the emanation the excited activity at once commences to decay. This excited activity is due to the deposit on the surface of bodies of active matter, which can be removed by solution in acid, and recovered on evaporation of the solvent. It has the property of concentrating itself on a negatively charged wire. Such a wire placed in the presence of the radium emanation becomes strongly active, and if drawn across a screen of zinc sulphide, some of the active matter is rubbed off, leaving a luminous trail.

[1] See Ramsay, *Journ. Chem. Soc.*, 1907, **91**, 931.

[2] Cameron and Ramsay, *Journ. Chem. Soc.*, 1907, **91**, 1266.

It has been ascertained that the deposited active matter from the radium emanation breaks up rapidly in successive and well-marked stages, yielding three ephemeral substances which have been named radium A, radium B, and radium C; the first of these emits α rays only, the last emits rays of all three kinds, and radium B emits β and γ rays. The emanation is half transformed in 3·85 days: radium A is half transformed in three minutes, radium B takes 26·7 minutes, and radium C 19·5 minutes for half transformation into a comparatively permanent product radium D. This requires 16·5 years for half transformation into radium E, half of which is transformed in 5 days into radium F. The complex nature of radium C has already been discussed (p. 1426).

660 *Radium F, Polonium, Radio-tellurium.* — During the investigation of the pitchblende residues from which radium was isolated, Mme. Curie obtained a second radioactive element to which the name of polonium was given. This substance was found by Mme. Curie to separate out with bismuth. She employed three methods of separation:

(*a*) Sublimation of the sulphides in vacuo: the active sulphide is the most volatile.

(*b*) Precipitation of the nitrate by water: the precipitate is the most active.

(*c*) Precipitation of a strongly acid solution of the chlorides by sulphuretted hydrogen: the precipitate is the most active.

Marckwald[1] obtained a radioactive substance with tellurium as an impurity, which he called radiotellurium. It is undoubtedly the same as polonium. Marckwald finds that if a plate of bismuth be immersed in a solution containing polonium the active matter is deposited on the plate, and the solution remains inactive. The active matter is also precipitated by treating the solution with stannous chloride. From fifteen tons of pitchblende Marckwald obtained sixteen grams of mixed selenium, tellurium, and polonium, from which, by treatment of the oxides with ammonia, an insoluble residue weighing three milligrams and containing all the active matter was obtained.

The radiation is extremely active, consisting entirely of α rays. One-hundredth of a milligram produces intense phos-

[1] *Ber.*, 1902, **35**, 2285, 4239; 1903, **36**, 2662.

phorescence in a screen of zinc sulphide. The period of half transformation is 136 days, and in this respect and in the nature of its radiation polonium agrees exactly with radium F, with which it is doubtless to be identified.

Marckwald[1] considers that radio-tellurium or polonium will prove to be the missing element of the sulphur-selenium-tellurium family, whilst Mme. Curie considers that it is more closely related to bismuth.

The atomic weight of polonium is probably about 210. Since it has been identified with radium F, and in the changes from radium into radium F four α particles are expelled, its atomic weight ought to be less than that of radium by fifteen or sixteen units if the α particle be helium. The unknown radium G may then very probably prove to be lead.

The properties of the various transformation products of radium are summarised in tabular form on p. 1444.

The lead salts separated from pitchblende are also radioactive, but it has been shown that they owe their activity to the presence of the transformation products of radium known as radium D, E, and F.

Recently a new method of separating polonium from lead and radium D by dialysis has been devised by Paneth,[2] who finds that polonium in solution behaves like a colloid and cannot diffuse through a membrane made of bladder or parchment. Making use of this property it is possible to separate polonium from lead salts and other impurities.

ACTINIUM.

661 Actinium, discovered by Debierne,[3] is, no doubt, the same substance as that described by Giesel[4] under the name of emanium. It was discovered in the precipitate of rare earths separated from pitchblende, the bulk of which consisted of thoria, and was finally obtained mixed with lanthana. It gives a characteristic emanation, and imparts activity to neighbouring objects.

Debierne has shown that actinium, like radium, gives rise

[1] *Ber.*, 1905, **38**, 591. [2] *Monatsh.*, 1913, **34**, 401.
[3] *Compt. rend.*, 1899, **129**, 593; 1900, **130**, 206; 1903, **136**, 446, 767.
[4] *Ber.*, 1902, **35**, 3608; 1903, **36**, 342; 1904, **37**, 1696, 3963.

to helium proportionate in quantity to the activity of the preparation.

The present state of knowledge regarding actinium is summarised in the table on p. 1444.

Boltwood[1] has shown that the amount of actinium present in uranium minerals is approximately proportional to the uranium content of the mineral. This fact suggests a genetic connection between actinium and uranium. But actinium appears not to be in the direct series of disintegration of uranium, and Rutherford has suggested that it forms the starting point of a branch series. The connection between uranium and actinium is, however, not yet fully understood.

THORIUM.

662 As already mentioned, the radioactivity of thorium was discovered by Schmidt and by Mme. Curie, and the existence of an emanation by Rutherford (p. 1424).

Rutherford and Soddy,[2] by adding ammonia to a solution of a thorium salt, so as to precipitate the thorium as hydroxide, found that the filtrate contained a substance many times more active than the thorium itself. This active constituent they named thorium X: in a month's time it had completely lost its activity, while the thorium had completely recovered its original activity. The decay of activity of the thorium X, and the recovery of the activity of the thorium, are found to be represented by exactly similar curves; the time required for decay to half value, or for the recovery of half the lost activity, being in each case 3·7 days.

Thorium X appears not to be formed directly from thorium, but through three intermediate products, mesothorium 1, mesothorium 2, and radiothorium.[3] Radiothorium cannot be separated from thorium by any known chemical process, nor can mesothorium 1 be separated from thorium X; but the first two substances can be separated from the second two by adding excess of ammonia to a solution of thorium nitrate. The further changes undergone by this substance are summarised on p. 1444.

[1] *Amer. J. Sci.*, 1908, **25**, 269.

[2] *Phil. Mag.*, 1906, [6], **4**, 370, 569.

[3] Hahn, *Proc. Roy. Soc.*, 1905, A, **76**, 115; *Ber.*, 1907, **40**, 1462; *Physikal. Zeit.*, 1907, **8**, 277; *ibid.*, 1908. **9**, 246.

Thorium, radium, and actinium exhibit many points of similarity; each gives an emanation whose life is short; these emanations have no definite combining properties, but belong, probably, to the helium-argon group of inert gases; in each case the emanation gives rise to a non-volatile substance (thorium A, radium A, actinium A) which deposits on the surface of bodies, and is concentrated on the negative electrode in an electric field. The emanations and the subsequent disintegration products show very striking analogies both with regard to the radiations emitted by each product and other properties. This can be seen from the table given on p. 1444.

URANIUM.

663 The discovery of the radioactivity of uranium by H. Becquerel in 1896 was, as already mentioned (p. 1407), the starting point of the series of brilliant investigations by which the science of radioactivity has been established. There is strong evidence derived from the radioactive properties of uranium that this body really consists of two distinct elements which, however, are so similar to each other as to be inseparable by chemical methods. The evidence rests on the fact, first noticed by Boltwood and subsequently confirmed by Geiger and Rutherford,[1] that an atom of uranium appears to give out two α particles during the disintegration instead of one, as is the case with most radioactive atoms emitting α rays. This fact can only be explained either by supposing uranium to consist of two successive disintegration products, or by assuming that an atom of uranium gives out two α particles simultaneously. The latter hypothesis has been disproved by Marsden and Barratt,[2] and Geiger and Nuttall[3] have shown that the α particles are not homogeneous. The two types of uranium are known as uranium 1 and uranium 2, the period of transformation of one of which is 5×19^9 years.

Von Hevesy[4] has shown that the valencies of the radio-elements can be found by observations on their rates of diffusion and mobilities in solution. It is shown that at any

[1] *Phil. Mag.*, 1910, **20**, 691. [2] *Proc. Phys. Soc.*, 1911, **23**, 367.
[3] *Phil. Mag.*, 1912, **23**, 439. [4] *Phil. Mag.*, 1913, **25**, 390.

rate in many cases the expulsion of an α particle by a parent substance gives rise to a change of valency of two units in the resulting product; but there is as yet insufficient evidence to say whether or not this rule is without exception. It has been shown by von Hevesy and von Putnoky [1] that uranium 1 and uranium 2 cannot be separated by diffusion, and that uranium 2, if it exists, is not only very similar to uranium 1, but has also the same valency as that element. Uranium 2 passes into uranium X, which can be chemically separated from uranium in several ways. Thus Crookes showed [2] that by a single chemical operation, viz., by precipitating a uranium salt with ammonium carbonate in excess, the whole of the photographic activity was concentrated in the precipitate, and the uranium left in solution was photographically inactive. The precipitate containing UrX was, photographically, many hundred times as active as the uranium from which it had been separated. Becquerel [3] found that on adding barium chloride to a solution of uranium salt and precipitating as barium sulphate, the precipitate was strongly active, photographically, and the uranium had lost its activity. A year later it was found that the barium had become inactive, whilst the uranium had completely regained its activity.

The uranium deprived of uranium X, although photographically inactive, is electrically active, this being due to the fact that the α particle which it emits is incapable of producing much photographic action. Uranium X can also be separated from uranium salts by boiling with lampblack, which retains this product.[4] Uranium X emits only β and γ rays and passes into ionium, possibly through an unknown product, uranium X_2, the period of half transformation being 22 days.

664 *Relation of Uranium and Radium.*—The further history of the transformation of uranium is interesting, for many facts point to the conclusion that radium is one of its transformation products. This was first surmised from the fact that the radioactivity of the uranium minerals is proportional to the quantity of uranium present [5] (in the absence of thorium). The ratio of uranium to radium in such minerals is almost

[1] *Phil. Mag.*, 1913, **25**, 415. [2] *Proc. Roy. Soc.*, 1900, **66**, 409.
[3] *Compt. rend.*, 1900, **131**, 137; 1901, **133**, 977.
[4] Becquerel, *Compt. rend.*, 1905, **141**, 485.
[5] McCoy, *Ber.*, 1904, **37**, 2641.

constant,[1] and these facts are most readily explained by the supposition that the radium is actually formed from the uranium. The production of radium from uranium has been measured by Soddy,[2] and by Boltwood,[3] who carefully freed uranium from radium and measured by the emanation test the amount of radium present after the lapse of a year or two. It was found that the rate of production of radium was far less than was to be expected if radium were formed directly from uranium. This seemed to indicate the existence of an intermediate product of slow rate of decay. This product has since been separated from carnotite by Boltwood,[4] who gave it the name *ionium*. This element is the direct predecessor of radium in the disintegration series. From measurements on the rate of growth of radium from uranium Soddy[5] suggests that the half-value period of ionium is of the order 100,000 years. This value is confirmed by Geiger and Nuttall, who, having determined the range of the α particle from polonium, deduced its half-value period from their rule (p. 1419). It is, however, noteworthy that Exner and Haschek,[6] and, independently, Russell and Rossi[7] failed to detect spectroscopically the presence of ionium in pitchblende residues, which must have contained about 10 per cent. of ionium if the period of transformation given above is correct, and if there is no other product between UrX and polonium. The experiments therefore seem to indicate the existence of a product of long life between UrX and ionium.

It is further supposed, as already mentioned, that lead may be one of the ultimate products of the transformation of radium, but the evidence on this point cannot be regarded as conclusive.

665 The following tables summarise our present knowledge of the active products of disintegration of the radio-elements. The column headed *half-value period* gives the time of falling to half activity, or the time required for half the substance to be transformed into the next product.

[1] Strutt, *Proc. Roy. Soc.*, 1905, **76**, A, 88, 312; Boltwood, *Phil. Mag.*, 1905, [6], **9**, 599.

[2] *Phil. Mag.*, 1905, [6], **9**, 768; 1908, **16**, 632; 1909, **18**, 846; 1910, **20**, 340.

[3] *Amer. J. Sci.*, 1905, **20**, 239.

[4] *Amer. J. Sci.*, 1906, **22**, 537; 1907, **24**, 370; 1908, **25**, 365.

[5] *Phil. Mag.*, 1909, **18**, 858.

[6] *Sitzungsber. K. Akad. Wiss. Wien*, 1912, IIa, **121**, 1075.

[7] *Proc. Roy. Soc.*, 1912, A, **87**, 478.

URANIUM RADIUM SERIES.

Product.	Half-value Period.	Rays emitted.	Group in Periodic Table to which Product belongs.
Uranium 1	5×10^9 years	α	VI*A*
Uranium X_1	24·6 days	β, γ	IV*A*
Uranium X_2 (?)	—	—	—
Uranium 2	2×10^6 years	α	VI*A*
Uranium Y^* (?)	1·5 days	β	—
Ionium	—	α	IV*A*
Radium	2×10^3 years	α, β	II*A*
Radium emanation	3·85 days	α	0
Radium *A*	3·0 minutes	α	—
Radium *B*	26·7 minutes	β, γ	—
Radium C_1	19·5 minutes	α, β, γ	—
Radium C_2*	1·4 minutes	β	
Radium *D*	16·5 years	β	IV*B*
Radium *E*	5 days	β, γ	V*B*
Radium *F* (Polonium)	136 days	α	VI*B*

THORIUM SERIES.

Product.	Half-value Period.	Rays emitted.	Group in Periodic Table to which Product belongs.
Thorium	$1{\cdot}3 \times 10^{10}$ years	α	IV*A*
Mesothorium 1	5·5 years	rayless	II*A*
Mesothorium 2	6·2 hours	β, γ	III*A*
Radio-thorium	2 years	α	IV*A*
Thorium *X*	3·7 days	α	II*A*
Thorium emanation	53 seconds	α	0
Thorium *A*	0·14 second	α	—
Thorium *B*	10·6 hours	β	—
Thorium C_1	60 minutes	α, β	—
Thorium C_2*	very short	α	
Thorium *D*	3·1 minutes	β, γ	III*b*

ACTINIUM SERIES.

Product.	Half-value Period.	Rays emitted.	Group in Periodic Table to which Product belongs.
Actinium	—	rayless	III*A*
Radio-actinium 1	19·5 days	—	—
Radio-actinium 2	—	—	—
Actinium *X*	11·6 days	α, β	II*A*
Actinium emanation	3·9 seconds	α	0
Actinium *A*	0·002 second	α	—
Actinium *B*	36·3 minutes	β	—
Actinium *C*	2·15 minutes	α	—
Actinium *D*	4·71 minutes	β, γ	III*B*

Products marked with an asterisk are branch products.

666 The discovery that the atoms of certain elements undergo continuous spontaneous disintegration with formation of substances of lower atomic weight necessitates a profound modification of the conception of the chemical atom which has hitherto been accepted. The corpuscular theory of matter (p. 39) has paved the way for such a modification by regarding the atom as containing a number of electrons, although recent work indicates that the number of these present in an atom is much smaller than was at first thought and is of the order of the number expressing the mass of the atom in multiples of that of hydrogen.[1]

The atom must now be regarded as an aggregate of simpler forms of matter, possessing enormous potential energy. This aggregate may, under conditions which we are not yet able to control, break down into simpler forms, a large amount of energy being evolved in the change. Hence the idea of the unalterability of the atom postulated by Dalton must be modified, and the atom must be regarded as a complex, but of a higher order than the chemical compounds formed by the union of atoms with each other. It is impossible at present to establish a more precise characterisation of this higher order of complex substances than is expressed in the statement that the decomposition of the atom is beyond our control and that the energy changes are of a higher order of magnitude than is the case with ordinary compounds.

These discoveries, however, whilst opening out new views as to the constitution of matter, are in no degree inconsistent with the well-established facts of chemical combination or with the application to them of Dalton's atomic theory.

[1] J. J. Thomson, *Phil. Mag.*, 1906, [6], 11, 769.

INDEX

INDEX

A

Absorption spectra, 163
Acid bronze, 718
Acid-forming oxides, 104
Acid salts, 108
Acids and alkalis, 91
Acids, bases, and salts, 90
Acids, nature of, 98
Actinium, 1428, 1439
Aich's metal, 651
Aikinite, 999
Alabanite, 1124, 1149
Albite, 711
Alembroth, 691
Algaroth, powder of, 982
Algodonite, 439
Alkali manufacture, 280
Alkali metals, 225
Alkali waste, 287, 297, 301
Alkaline earth metals, 529
Alkalis, 225
Alkalis and acids, 91
Allemontite, 964, 993
Alloys, 74, 76; conductivity of, 86; constitution of, 82; microscopical study of, 81; solubility of, 87; thermal classification of, 77
Almandine, 711
Alstonite, 602, 613
Alum, 710
Aluman, 718
Alum-cake, 730
Alumina, 718
Aluminates, 724
Aluminite, 730
Aluminium, 710; alloys of, 717; annual output of, 713; atomic weight of, 750; compounds of, 718; detection of, 749; electrolytic production of, 712; estimation of, 750; preparation of, 711; properties of, 714; uses of, 716
Aluminium amalgam, 718
Aluminium bromide, 727
Aluminium bronze, 717
Aluminium carbide, 738
Aluminium chloride, 726; vapour density of, 33
Aluminium chlorosulphate, 730
Aluminium fluoride, 725
Aluminium group, 709
Aluminium hydroxides, 720
Aluminium iodide, 728
Aluminium nitrate, 737
Aluminium nitride, 737
Aluminium oxide, 718
Aluminium peroxide, 724
Aluminium phosphates, 738
Aluminium phosphides, 738
Aluminium silicates, 739
Aluminium sulphate, 729
Aluminium sulphide, 728
Alum-stone, 731
Alums, 730
Alunite, 731
Amalgams, 88, 678
Ammiolite, 977
Ammonal, 717
Ammonia alum, 736
Ammonia-soda process, 304
Ammoniacal derivatives of cobalt, 1288; of copper, 442; of iridium, 1369; of palladium, 1346; of platinum, 1398; of rhodium, 1334; of ruthenium, 1326
Ammoniacal liquor, 380
Ammonium amalgam, 377
Ammonium antimonate, 980
Ammonium aurichloride, 516
Ammonium aurocyanide, 524
Ammonium azoimide, 389
Ammonium bromide, 383
Ammonium carbonates, 391
Ammonium chlorate, 383
Ammonium chloride, 380
Ammonium chromate, 1031
Ammonium chromic sulphate, 1045

Ammonium compounds, 376
Ammonium cyanate, 394
Ammonium cyanide, 393
Ammonium dichromate, 1031
Ammonium ferricyanide, 1258
Ammonium ferrocyanide, 1255
Ammonium fluoride, 379
Ammonium hydrosulphide, 384
Ammonium iodide, 219, 383
Ammonium iridichloride, 1366
Ammonium iridiobromide, 1366
Ammonium molybdates, 1068
Ammonium nitrate, 390
Ammonium nitrite, 389
Ammonium osmichloride, 1355
Ammonium osmochloride, 1354
Ammonium palladichloride, 1343
Ammonium palladiochloride, 1343
Ammonium perchlorate, 383
Ammonium permanganate, 1144
Ammonium peroxide, 379
Ammonium persulphate, 389
Ammonium phosphates, 390
Ammonium phosphomolybdate, 1071
Ammonium platinichloride, 1394
Ammonium platinochloride, 1391
Ammonium plumbichloride, 893
Ammonium polysulphides, 385
Ammonium rhodochloride, 1333
Ammonium selenate, 389
Ammonium stannichloride, 864
Ammonium sulphate, 218, 385
Ammonium sulphide, 384
Ammonium thioantimonate, 991
Ammonium thiocyanate, 394
Ammonium thiomolybdate, 1079
Ammonium thiovanadate, 936
Ammonium titanofluoride, 814
Ammonium tritantalate, 959
Ammonium tungstates, 1090
Ammonium uranate, 1110
Ammonium vanadite, 929
Ammonium vanadium alum, 938
Amphoteric hydroxides, 106
Analysis, crystallochemical, 204
Anatase, 806, 809
Andradite, 711
Anglesite, 873, 896
Anhydrite, 530, 552
Annabergite, 1298
Anomalies of periodic system, 69
Antifriction metal, 971
Antimonates, 978
Antimonial copper, 964
Antimonial nickel, 964
Antimonial saffron, 991
Antimonial silver, 964
Antimonic acids, 977
Antimonious acid, 975
Antimonite, 962
Antimony, 962; alloys of, 970; atomic weight of, 998; detection of, 994; estimation of, 996; medicinal uses of, 993; modifications of, 968; preparation of, 964; properties of, 967; uses of, 969
Antimony arsenide, 993
Antimony blende, 991
Antimony chlorosulphides, 992
Antimony cinnabar, 988
Antimony hydride, 971
Antimony iodosulphides, 992
Antimony ochre, 964
Antimony oxides, 973
Antimony oxysulphide, 991
Antimony pentachloride, 983
Antimony pentafluoride, 980
Antimony pentasulphide, 989
Antimony pentiodide, 985
Antimony pentoxide, 977
Antimony phosphide, 993
Antimony poisoning, 994
Antimony selenides, 992
Antimony sulphate, 992
Antimony telluride, 993
Antimony tetrachloride, 984
Antimony tetroxide, 976
Antimony thiophosphate, 993
Antimony tribromide, 984
Antimony trichloride, 981
Antimony trifluoride, 980
Antimony tri-iodide, 985
Antimony trioxide, 974
Antimony trisulphide, 985
Apatite, 530, 537, 558
Apjohnite, 1151
Apophyllite, 564
Aquochlororuthenates, 1324
Aragonite, 190, 530, 561
Arc spectra, 146
Argentan, 718, 1302
Argentiferous copper, 455
Argentite, 445, 475
Argon, atomic weight of, 67
Argyrodite, 838, 839
Arsenical pyrites, 1165, 1173
Arsenovanadic acid, 940
Asbestos, 625
Astracanite, 118
Asymmetric system, 187
Atom, constitution of the, 39
Atom and molecule, 27
Atomic heat, 15, 66
Atomic volume, 57, 60
Atomic weight, selection of, 13
Atomic weights, basis of, 9; correction of doubtful, 66; determination of, 6; revision of, 13
Auribromic acid, 517
Auric bromide, 517
Auric chloride, 514
Auric cyanide, 524
Auric hydroxide, 512
Auric iodide, 518
Auric oxide, 512
Auric sulphide, 519
Auric thiocyanate, 525
Aurichalcite, 644

Aurichloric acid, 515
Auricyanic acid, 524
Auroauric oxide, 513
Auroauric sulphide, 519
Aurodiamine, 521
Aurous acetylide, 523
Aurous bromide, 516
Aurous carbide, 523
Aurous chloride, 513
Aurous cyanide, 523
Aurous hydroxide, 511
Aurous iodide, 517
Aurous oxide, 511
Aurous sulphide, 518
Aurous thiocyanate, 524
Auryl hydroxide, 512
Austenite, 1216
Axes of symmetry, 183
Axial ratios, 179
Azurite, 400, 440

B

Balanced reactions, 128
Barium, 601; atomic weight of, 615; compounds of, 603; detection of, 614; estimation of, 615; occurrence of, 602; preparation of, 602; properties of, 603
Barium amide, 612
Barium azoimide, 612
Barium carbide, 613
Barium carbonate, 613
Barium chlorate, 608
Barium chloride, 606
Barium chromate, 1032
Barium cobaltite, 1281
Barium dioxide, 605
Barium disulphate, 611
Barium dithionate, 611
Barium ferrate, 1226
Barium ferrocyanide, 1256
Barium fluoride, 607
Barium hydride, 606
Barium hydrosulphide, 609
Barium hydroxide, 604
Barium iodate, 608
Barium iodide, 607
Barium iridicyanide, 1369
Barium manganate, 1140
Barium molybdates, 1069
Barium monoxide, 604
Barium nickelite, 1306
Barium nitrate, 612
Barium nitride, 611
Barium nitrite, 612
Barium osmocyanide, 1359
Barium percarbonate, 614
Barium permanganate, 1144
Barium persulphate, 611
Barium platinocyanide, 1402
Barium platinonitrite, 1398
Barium silicates, 614
Barium subchloride, 607
Barium suboxide, 603
Barium sulphate, 214, 610
Barium sulphide, 608
Barium tetrasulphide, 609
Barium thioantimonate, 991
Barlow and Pope's theory, 220
Baryta, 604
Baryta water, 605
Baryto-calcite, 602, 613
Baryto-celestine, 595, 602
Bases, acids, and salts, 90
Basic oxides, 103
Basic salts, 108
Bauxite, 710, 720, 721
Becquerel rays, 1413
Bell metal, 850
Beraunite, 1246
Berthierite, 964
Beryl, 192, 617
Beryllium, 616
Bessemer steel, 1203
Biotite, 711
Bismuth, 998; alloys of, 1003; atomic weight of, 1016; detection of, 1014; estimation of, 1015; metallurgy of, 999; properties of, 1002
Bismuth arsenate, 1014
Bismuth-aurite, 491
Bismuth carbonate, 1014
Bismuth chlorosulphide, 1010
Bismuth chromate, 1034
Bismuth dichloride, 1007
Bismuth nitrate, 1011
Bismuth nitride, 1011
Bismuth ochre, 999, 1005
Bismuth oxybromide, 1008
Bismuth oxychloride, 1007
Bismuth oxyfluoride, 1007
Bismuth oxyiodide, 1009
Bismuth oxysulphides, 1010
Bismuth phosphate, 1013
Bismuth selenide, 1011
Bismuth silicate, 1014
Bismuth suboxide, 1004
Bismuth subsulphide, 1009
Bismuth sulphate, 1010
Bismuth telluride, 1011
Bismuth thiosulphate, 1011
Bismuth tribromide, 1008
Bismuth trichloride, 1007
Bismuth trifluoride, 1007
Bismuth trihydroxide, 1006
Bismuth tri-iodide, 1008
Bismuth trioxide, 1005
Bismuth trisulphide, 1009
Bismuthic acid, 1006
Bismuthite, 999, 1009, 1014
Bismutosmaltite, 999
Bitter-spar, 530
Black-ash process, 291
Black band iron-stone, 1175
Black-jack, 644

Blanc fixé, 611
Blast furnace, 1178; chemical changes in, 1183; gases of the, 1185
Bleaching powder, 539, 541
Bleaching processes, 549.
Bleinierite, 980
Blister copper, 404
Blood, spectrum reaction of, 167
Blue John, 536
Blue vitriol, 434
Boiling points of the elements, 62
Bone-phosphate, 558
Bones, constituents of, 558
Bononian phosphorus, 609
Boracite, 330
Borax, 271
Borax glass, 271
Boronatrocalcite, 271
Boulangerite, 964
Bournonite, 872, 964
Brass, 651
Braunite, 1124, 1131
Breithauptite, 964, 1298
Brewsterite, 595, 602
Brine, electrolysis of, 313; evaporation of, 251
Brine wells, 250
Britannia metal, 970
Bromargyrite, 471
Bronze, 850
Brookite, 806, 809
Brown-spar, 530
Brucite, 629
Brunswick green, 433
Butter of antimony, 981
Butter of tin, 863
Buttercup yellow, 1033

C

Cadmium, 664; atomic weight of, 670; detection of, 669; estimation of, 670; preparation of, 664; properties of, 665
Cadmium carbonates, 669
Cadmium chloride, 667
Cadmium hydroxide, 666
Cadmium iodide, 668
Cadmium nitrate, 669
Cadmium oxide, 666
Cadmium sulphate, 668
Cadmium sulphide, 668
Cadmous hydroxide, 667
Cadmous oxide, 667
Cæsium, 372; atomic weight of, 375; detection of, 375; discovery of, 161; properties of, 373; occurrence of, 372; separation of, 367
Cæsium compounds, 374, 375
Cæsium platinichloride, 1394
Cæsium sulphate, 218
Calamine, 644, 660
Calaverite, 491
Calcium, 530; atomic weight of, 594; detection of, 593; estimation of, 593; preparation of, 531; properties of, 532; occurrence of, 530
Calcium arsenide, 559
Calcium bisulphite, 552
Calcium boride, 559
Calcium borosilicates, 565
Calcium bromide, 539
Calcium carbide, 560
Calcium carbonate, 561; dissociation of, 129
Calcium chlorate, 550
Calcium chloride, 537
Calcium cyanamide, 564
Calcium dioxide, 535
Calcium disulphide, 551
Calcium ferrite, 1225
Calcium ferrocyanide, 1255
Calcium fluoride, 536
Calcium hydride, 536
Calcium hydrosulphide, 551
Calcium hydroxide, 535
Calcium hydroxyhydrosulphide, 551
Calcium hypophosphite, 559
Calcium hyposulphite, 552
Calcium iodide, 539
Calcium molybdates, 1068
Calcium monosulphide, 550
Calcium monoxide, 532
Calcium nitrate, 556
Calcium nitride, 556
Calcium pentasulphide, 551
Calcium phosphates, 557
Calcium phosphide, 557
Calcium silicates, 564
Calcium silicide, 564
Calcium subchloride, 539
Calcium sulphate, 552
Calcium sulphite, 551
Calcium thiosulphate, 556
Calcium titanate, 811
Calcium titanosilicate, 812
Calcium tungstate, 1090
Calcspar, 530, 561
Caliche, 262
Calomel, 684, 704
Campylite, 899
Canton's phosphorus, 550
Carbides, 127
Carbonates, 127
Carbonylferrocyanic acid, 1266
Carbonylplatinochlorides, 1390
Carnallite, 119, 319, 330, 367, 625, 631
Carnotite, 913, 1105
Case hardening, 1213
Cassel yellow, 893
Cassiterite, 197, 214, 843, 854
Cast iron, 1172, 1176, 1187, 1190
Castner's process, 239
Catalytic action, 133
Caustic potash, 325
Caustic soda, 244, 299, 317

Celestine, 594
Celtium, 802
Cementation process, 1199
Cements, 565
Centre of symmetry, 184
Ceric fluoride, 794
Ceric nitrate, 795
Ceric sulphate, 794
Cerite, 774, 766
Cerium, 788, 789; atomic weight of, 796; detection of, 795; estimation of, 796
Cerium carbide, 795
Cerium oxides, 790
Cerium silicide, 795
Cerous bromide, 792
Cerous carbonate, 793
Cerous chloride, 791
Cerous hydride, 791
Cerous hydroxide, 790
Cerous iodide, 792
Cerous nitrate, 793
Cerous nitride, 793
Cerous phosphate, 793
Cerous sulphate, 792
Cerous sulphide, 792
Cerussite, 872, 899
Cervantite, 964, 976
Chalcocite, 400
Chalcopyrite, 400
Chalk, 530, 561
Chalybite, 530
Chance process, 301
Chemical analysis by positive rays, 1410
Chili saltpetre, 262
Chloanthite, 1312
Chlorargyrite, 445, 467
Chlorates, 124
Chloride of lime, 539
Chlorides, 122
Chloroauric acid, 515
Chloropalladates, 1343
Chloropalladites, 1343
Chloroplatinic acid, 1393
Chloroplatinites, 1391
Chloroplatinophosphorous acids, 1390
Chlororhodites, 1333
Chlororuthenates, 1324
Chlororuthenites, 1324
Chromammines, 1055
Chrome alum, 1044
Chrome iron stone, 1019, 1028, 1058
Chrome ochre, 1022
Chrome orange, 1034
Chrome red, 1033
Chrome yellow, 1033
Chromic acid, 1027
Chromic anhydride, 1025
Chromic bromide, 1043
Chromic chloride, 1041
Chromic chromate, 1034
Chromic fluoride, 1041
Chromic hydroxides, 1023
Chromic nitrate, 1049
Chromic oxide, 1022
Chromic phosphates, 1049
Chromic sulphate, 1044
Chromic sulphide, 1044
Chromic thiocyanate, 1050
Chromite, 1019
Chromites, 1024
Chromitite, 1019
Chromium, 1019; ammoniacal compounds of, 1051; asymmetric compounds of, 1056; atomic weight of, 1058; detection of, 1057; estimation of, 1058; preparation of, 1020; properties of, 1021
Chromium amalgams, 1021
Chromium borides, 1049
Chromium carbides, 1050
Chromium dioxide, 1034
Chromium group, 1017
Chromium monoxide, 1022
Chromium nitride, 1048
Chromium phosphide, 1049
Chromium sesquioxide, 1022
Chromium silicides, 1051
Chromium trioxide, 1025
Chromosulphuric acids, 1047
Chromous acetate, 1040
Chromous bromide, 1040
Chromous carbonate, 1040
Chromous chloride, 1039
Chromous hydroxide, 1022
Chromous iodide, 1040
Chromous sulphate, 1040
Chromous sulphide, 1040
Chromyl dichloride, 1035
Chromyl difluoride, 1035
Chromylamide, 1037
Chrysoberyl, 617
Chrysocolla, 441
Cinnabar, 672, 693
Classification of the elements, 42, 44
Claus kiln, 302
Clay iron-stone, 1175, 1177
Clays, 711
Clinoclasite, 440
Cobalt, 1274; atomic weight of, 67, 1296; detection of, 1296; estimation of, 1296; preparation of, 1276; properties of, 1277
Cobalt and nickel, separation of, 1316, 1317
Cobalt antimonides, 1292
Cobalt arsenates, 1292
Cobalt arsenides, 1291
Cobalt azoimide, 1286
Cobalt bloom, 1275
Cobalt bromide, 1283
Cobalt carbonates, 1292
Cobalt carbonyls, 1292
Cobalt chlorate, 1283
Cobalt chloride, 1281
Cobalt dioxide, 1280
Cobalt glance, 1275, 1291

Cobalt iodate, 1283
Cobalt iodide, 1283
Cobalt nitrate, 1287
Cobalt nitride, 1286
Cobalt nitrite, 1286
Cobalt phosphates, 1292
Cobalt phosphides, 1291
Cobalt silicates, 1295
Cobalt silicides, 1294
Cobalt sulphide, 1284
Cobalt tetracarbonyl, 1292
Cobalt tricarbonyl, 1293
Cobalt ultramarine, 1295
Cobaltammine salts, 1288
Cobaltic ammonium alum, 1285
Cobaltic fluoride, 1281
Cobaltic hydroxide, 1279
Cobaltic oxide, 1279
Cobaltic sulphite, 1284
Cobalticyanic acid, 1294
Cobaltite, 1275, 1291
Cobalto-cobaltic oxide, 1279
Cobaltous cobalticyanide, 1294
Cobaltous cobaltite, 1281
Cobaltous cyanide, 1293
Cobaltous fluoride, 1281
Cobaltous hydroxide, 1278
Cobaltous oxide, 1278
Cobaltous sulphate, 1284, 1285
Cobaltous sulphite, 1284
Coinage, gold, 510
Coinage, silver, 463
Colcothar, 1222
Collargol, 460
Colloidal solutions of metals, 72
Cologne yellow, 1033
Columbic acid, 951
Columbite, 944, 946
Columbium, 944; atomic weight of, 956; detection of, 955; estimation of, 955; preparation of, 949; properties of, 949
Columbium compounds, extraction of, 948
Columbium nitride, 955
Columbium oxides, 950
Columbium oxybromide, 954
Columbium oxychloride, 954
Columbium oxyfluoride, 952
Columbium oxysulphide, 955
Columbium pentabromide, 954
Columbium pentachloride, 953
Columbium pentafluoride, 952
Columbium trichloride, 953
Common salt, 250
Complex salts, 109
Compressible atoms, theory of, 61
Conductivity of alloys, 86; metals, 64
Condy's fluid, 1144
Constantan, 1304
Contra-valency, 41
Constitution of the atom, 39
Co-ordination compounds, 38
Copiapite, 1239
Copper, 398; alloys of, 418; ammoniacal compounds, 442; annual production of, 418; atomic weight of, 444; colloidal, 420; detection of, 443; electrolytic refining of, 416; estimation of, 444; ores of, 400; properties of, 418; sources of, 399; uses of, 420; wet extraction of, 413
Copper arsenates, 440
Copper arsenides, 439
Copper carbonates, 440
Copper chromates, 1031
Copper dioxide, 426
Copper ferrocyanide, 1257
Copper glance, 400
Copper oxides, 421
Copper oxychloride, 433
Copper peroxide, 425
Copper phosphides, 431
Copper polysulphides, 434
Copper pyrites, 400, 1165
Copper quadrantoxide, 425
Copper silicates, 441
Copper smelting, 400, 408
Copper sulphate, 434
Copper trientoxide, 425
Coprolites, 558
Coral, 530
Correction of doubtful atomic weights, 66
Corrosive sublimate, 688, 704
Corpuscles, 40
Corundum, 710, 718
Cotunnite, 892
Covellite, 400, 434
Crocoisite, 873, 1019
Crocus, 1222
Crocus antimonii, 991
Crookesite, 759
Cryolite, 711, 725
Cryolite soda process, 303
Crystal carbonate, 275, 316
Crystalline form of metals, 71
Crystallochemical analysis, 204
Crystallographic axes, 179; systems, 186
Crystallography, 174; chemical, 208
Crystal structures, theories of, 220
Crystals, characteristics of, 175; classes of, 185, 200; distortion of, 176; measurements of, 176; optical properties of, 199; pyroelectric behaviour of, 200; structure of, 204; symmetry of, 182; thermal properties of, 199
Cubic system, 193, 201
Cupric arsenite, 439
Cupric bromide, 433
Cupric chloride, 432
Cupric fluoride, 432
Cupric hydride, 432
Cupric hydroxide, 424

Cupric nitrate, 437
Cupric nitrite, 438
Cupric oxide, 423
Cupric phosphate, 439
Cupric phosphide, 438
Cupric sulphate, 434
Cupric sulphide, 434
Cuprite, 400, 421
Cuproscheelite, 1083
Cuprous acetylide, 428
Cuprous bromide, 428
Cuprous chloride, 426; molecular formula of, 33, 35
Cuprous cyanide, 431
Cuprous fluoride, 426
Cuprous hydride, 426
Cuprous hydroxide, 422
Cuprous iodide, 428
Cuprous nitride, 430
Cuprous oxide, 421
Cuprous phosphide, 431
Cuprous sulphate, 430
Cuprous sulphide, 429
Cuprous sulphite, 429
Cuprous thiocyanate, 431
Cyanides, 123
Cyanides, complex, 1251

D

Daguerreotype process, 483
Damascening, 1213
Danburite, 565
Datolite, 565
Dechenite, 912
Descloizite, 912
Dialogite, 1155
Dianium, 946
Diaspore, 710, 720
Diffusion of metals, 86
Dilute solutions, constitution of, 100
Dioptase, 441
Disintegration theory, 1424
Dissociation, 129, 136; electrolytic, 100; hydrolytic, 102
Divanadyl hydroxide, 929
Dolomite, 530, 625, 640
Domeykite, 439
Double salts, 109, 118
Dualistic theory, 94
Dufrenite, 1245
Dulong and Petit's law, 16
Dung substitute, 270
Dutch brass, 651
Dutch white, 903
Dyscrasite, 445, 964
Dysprosium, 801

E

Earthenware, 741, 745
Eau de Javelle, 333
Ekaboron, 68
Ekaluminium, 68
Ekasilicon, 68
Electrochemical theory of valency, 39
Electrolysis of alkali salts, 97
Electrolysis of brine, 313
Electrolytic dissociation, 100
Electrolytic soda process, 311
Electrons, 40
Electro-nickel plating, 1301
Electrotyping process, 416
Elements, classification of, 42, 44
Elements in sun's atmosphere, 171
Emanation, 1424
Embolite, 471
Emerald copper, 441
Emery, 719
Emission spectra, 145
Emplectite, 999
Enamel, 588
Enantiomorphism, 195, 209
Epsom salts, 633
Epsomite, 625, 633
Equilibrium, 130, 134
Equilibrium constant, 134, 138
Equivalent, determination of the, 9
Erbium, 801
Erubescite, 400
Erythrite, 1275
Ethyl ferrocyanide, 1254
Euclase, 617
Eulytite, 999, 1014
Europium, 800
Eutectic mixtures of metals, 77, 83
Euxenite, 775, 830, 838, 947
Explosive antimony, 969

F

Faience, 746
Felspars, 711, 739
Ferberite, 1083
Fergusonite, 775, 947, 948
Ferric acid, 1225
Ferric ammonium sulphate, 1240
Ferric arsenates, 1246
Ferric arsenite, 1246
Ferric bromide, 1231
Ferric chloride, 1228; hydrates of, 116; vapour density of, 32
Ferric ferricyanides, 1265
Ferric ferrocyanides, 1260
Ferric fluoride, 1227
Ferric hydroxide, 1222
Ferric nitrate, 1241
Ferric oxide, 1221
Ferric oxychlorides, 1231
Ferric phosphates, 1245
Ferric potassium sulphate, 1240
Ferric sulphate, 1239
Ferric sulphide, 1233
Ferric thiocyanate, 1269
Ferricyanic acid, 1257

Ferricyanogen compounds, 1257
Ferrite, 1216
Ferrites, 1224
Ferrocyanic acid, 1253
Ferrocyanogen compounds, 1252
Ferrocyanogen radical, 1250
Ferromanganese, 1189
Ferropentacarbonyl, 1247
Ferrosilicon, 1270
Ferroso-ferric chloride, 1228
Ferroso-ferric fluoride, 1227
Ferroso-ferric oxide, 1219
Ferroso-ferric silicates, 1240
Ferrotetracarbonyl, 1248
Ferrous ammonium sulphate, 1238
Ferrous bicarbonate, 1247
Ferrous bromide, 1231
Ferrous carbonate, 1247
Ferrous chloride, 1227
Ferrous chromite, 1025
Ferrous cobalticyanide, 1294
Ferrous disulphate, 1259
Ferrous ferrocyanides, 1259
Ferrous fluoride, 1227
Ferrous hydroxide, 1219
Ferrous iodide, 1232
Ferrous nitrate, 1241
Ferrous oxide, 1218
Ferrous perchlorate, 1232
Ferrous phosphate, 1245
Ferrous sulphate, 1236
Ferrous sulphide, 1165, 1232
Ferrous sulphite, 1236
Ferrous thiocyanate, 1269
Ferrous tungstate, 1091
Fibro-ferrite, 1239
Fischer's salt, 1286
Flame spectra, 145
Fluorides, 122
Fluorspar, 193, 197, 536
Fowler's solution, 353
Fracture of metals, 71
Franklinite, 644, 1174
Fraunhofer's lines, 164, 168
Freezing-point curves for alloys, 77
Fulminating gold, 521
Fulminating platinum, 1398
Fulminating silver, 478
Fusible metal, 1003
Fusible white precipitate, 703

G

Gadolinite, 774, 776
Gadolinium, 800
Gahnite, 644, 724
Galena, 872, 895
Gallium, 68, 751; atomic weight of, 753; discovery of, 163; preparation of, 751; properties of, 752
Gallium compounds, 753
Garnet, 193, 711, 739
Garnierite, 1298, 1315
Germanium, 68, 838; atomic weight of, 841; detection of, 841; estimation of, 841; properties of, 838
Germanium chloroform, 840
Germanium dichloride, 841
Germanium fluoride, 840
Germanium hydride, 840
Germanium oxides, 839
Germanium oxychloride, 840
Germanium sulphides, 841
Germanium tetrachloride, 840
German silver, 1302, 1303
Gibbsite, 720
Gilding, 509
Glass, 567; coloured, 588; decomposition of, 586; history of, 568; manufacture of, 575; varieties of, 572
Glass of antimony, 991
Glauberite, 258, 556
Glauber's salt, 258
Glucina, 619
Glucinum, 616; atomic weight of, 67, 623; compounds of, 619; detection of, 623; estimation of, 623; preparation of, 617; properties of, 618
Glucinum borocarbide, 622
Glucinum bromide, 621
Glucinum carbide, 622
Glucinum carbonates, 622
Glucinum chloride, 621
Glucinum fluoride, 621
Glucinum hydroxide, 620
Glucinum iodide, 621
Glucinum nitrate, 622
Glucinum oxide, 619
Glucinum sulphates, 621
Göthite, 1222
Gold, 490; alloys of, 509; atomic weight of, 66, 526; colloidal, 507; compounds of, 511; detection of, 525; estimation of, 525; electrodeposition of, 509; extraction of, 495, 497; fulminating, 521; native, 495; occurrence of, 491, 492; preparation of pure, 504; properties of, 504; refining of, 501, 503; world's production of, 494
Gold-amalgam, 510
Gold bronze, 718
Gold bullion, assay of, 526
Gold coinage, 510
Gold ores, assay of, 525
Gold phosphides, 523
Gold telluride, 521
Goniometer, 177
Goslarite, 644, 658
Greenockite, 664, 668
Green vitriol, 1236
Grossular, 711
Guarinite, 812
Guignet's green, 1024

Gun-metal, 850
Gunpowder, 348
Gypsum, 530, 552

H

Hæmatite, brown, 1165, 1175, 1177; red, 1165, 1174, 1177
Hamburg white, 903
Hardenite, 1216
Harmotome, 602
Hatchett's brown, 1257
Hauerite, 1124, 1150
Haüyne, 749
Hausmannite, 1124, 1130
Helium, discovery of, 163
Helium from radium, 1432
Heavy spar, 602, 610
Hemihedral facets, 196
Hemimorphite, 644
Hercules metal, 718
Hexagonal system, 192, 201
Holmium, 801
Horn-quicksilver, 684
Horn-silver, 445, 467
Hübnerite, 1083, 1091
Hyacinth, 822, 828
Hyalophane, 602
Hydrargillite, 720
Hydrates and solubility, 113, 116
Hydraulic cement, 566
Hydraulic lime, 534
Hydraulic mortar, 565
Hydrazine, salts of, 396
Hydrohæmatite, 1222
Hydrolytic dissociation of salts, 102
Hydromagnesite, 639
Hydroxides, 103
Hydroxylamine, salts of, 395
Hydrozincite, 644
Hypochlorites, 124, 541
Hypovanadates, 929
Hypovanadic hydrate, 929
Hypovanadic sulphates, 938

I

Ilmenite, 805, 806, 812
Ilmenium, 946
Incandescent mantles, 832
Indicators, 100
Indices, 180
Indigo-copper, 434
Indium, 754; atomic weight of, 67, 758; detection of, 758; discovery of, 162
Indium ammonium alum, 757
Indium chlorides, 756
Indium compounds, 755
Indium hydroxide, 756
Indium iodide, 757
Indium fluoride, 757
Indium nitrate, 757
Indium oxide, 755
Indium sulphate, 757
Indium sulphide, 757
Indium sulphite, 757
Infusible white percipitate, 702
Intercepts, 179
Intermetallic compounds, 84
Iodargyrite, 473
Iodine, atomic weight of, 67
Iodostannic acid, 860
Iridibromides, 1367
Iridichlorides, 1366
Iridicyanic acid, 1368
Iridicyanides, 1368
Iridiochlorides, 1365
Iridionitrites, 1368
Iridium, 1349, 1360; ammoniacal derivatives of, 1369; atomic weight of, 66, 1370; detection and estimation of, 1370; preparation of, 1361; properties of, 1362
Iridium bromides, 1366
Iridium chlorides, 1365
Iridium hydroxides, 1364, 1365
Iridium iodide, 1367
Iridium oxides, 1364
Iridium sulphates, 1367, 1368
Iridium sulphides, 1367
Iridium sulphites, 1367
Iron, 1162; atomic weight of, 1274; compounds of, 1217; detection of, 1271; estimation of, 1272, 1273; grey, 1187; metallurgy of, 1171; meteoric, 1163; mottled, 1188; ores of, 1165, 1173; passive, 1167; preparation of pure, 1165; properties of, 1166; reduced, 1168; rusting of, 1168; spongy, 1168; varieties of, 1172; white, 1187
Iron alum, 1240
Iron amalgam, 1170
Iron arsenides, 1246
Iron borides, 1246
Iron carbide, 1247
Iron carbonyls, 1247, 1248
Iron cyanogen compounds, 1249
Iron disulphide, 1234
Iron, magnetic oxide of, 106, 1219
Iron nitrides, 1240
Iron, nitroso-compounds of, 1242
Iron pentacyano-compounds, 1266
Iron phosphides, 1243
Iron pyrites, 1165, 1173, 1235
Iron silicates, 1271
Iron silicides, 1270
Iron subsulphide, 1236
Isodimorphism, 219
Isomorphism, 24, 211, 213, 217
Isomorphous mixtures, 215, 216
Isomorphous series, 25

J

Jamesonite, 964
Johannite, 1118

K

Kainite, 330, 625
Kaolin, 739
Keilhauite, 774, 806
Keramohalite, 729
Kermesite, 991
Kieserite, 330, 625, 633
Kleinite, 691
Kupfernickel, 1297, 1298, 1312

L

Labile systems, 115
Labradorite, 711
Lanarkite, 873
Lanthanite, 788
Lanthanum, 785; atomic weight of, 788; detection of, 788; estimation of, 788
Lanthanum bromate, 787
Lanthanum carbide, 787
Lanthanum carbonate, 788
Lanthanum chloride, 786
Lanthanum hydride, 786
Lanthanum hydroxide, 785
Lanthanum nitrate, 787
Lanthanum nitride, 787
Lanthanum oxide, 785
Lanthanum sulphate, 786
Lanthanum sulphide, 786
Lapis lazuli, 746
Laurionite, 892
Laurite, 1319, 1325
Law of Dulong and Petit, 16
Law of geometrical crystallography, 178
Law of mass action, 128, 131
Law of octaves, 46
Law of rational intercepts, 180
Loadstone, 1174
Lorandite, 759
Lead, 871; action of water on, 904; atomic weight of, 908; compounds of, 885; detection of, 906; desilverisation of, 879; estimation of, 908; poisonous action of, 904; preparation of chemically pure, 883; properties of, 884; smelting of, 873; world's production of, 883
Lead antimonate, 980
Lead borates, 899
Lead bromide, 894
Lead carbonates, 899
Lead chloride, 891
Lead chromates, 1033
Lead cyanate, 903
Lead cyanide, 903
Lead ferricyanide, 1258
Lead fluorides, 891
Lead hydroxide, 886
Lead imide, 897
Lead iodide, 894
Lead molybdate, 1069
Lead monoxide, 885
Lead nitrate, 898
Lead nitrite, 897
Lead oxybromide, 894
Lead peroxide, 889
Lead persulphate, 897
Lead phosphates, 899
Lead sesquioxide, 887
Lead silicates, 903
Lead suboxide, 887
Lead sulphate, 896
Lead sulphide, 895
Lead tetrachloride, 893
Lead tungstate, 1091
Leadhillite, 873
Leblanc soda process, 283
Lemon chrome, 1032
Lepidolite, 227, 365
Leucophane, 617
Libethenite, 439
Lichtenberg's metal, 1003
Liebigite, 1105, 1120
Light, action of, on silver salts, 487
Lime, 532; superphosphate of, 559
Lime burning, 533
Limestone, 530, 533, 561
Limonite, 1175, 1222
Linnaeite, 1275, 1284, 1298, 1309
Lipowitz, 1003
Liquation in alloys, 85
Litharge, 886
Lithium, 227; atomic weight of, 237; detection of, 236; estimation of, 237; occurrence of, 160; preparation of, 229; properties of, 230; salts of, 232; sources of, 227; spectroscopic detection of, 160
Lithium amide, 233
Lithium azoimide, 234
Lithium carbide, 234
Lithium carbonate, 235
Lithium chloride, 232
Lithium hydride, 232
Lithium hydroxide, 231
Lithium imide, 234
Lithium iodotetrachloride, 233
Lithium nitrate, 234
Lithium nitride, 233
Lithium oxide, 231
Lithium peroxide, 232
Lithium phosphate, 234
Lithium platinichloride, 1393
Lithium silicates, 236
Lithium silicide, 236
Lithium sulphate, 233
Liver of sulphur, 339
Livers of antimony, 988
Lunar caustic, 479
Lutecium, 802

M

Magistery of bismuth, 1012
Magnalium, 626, 718
Magnesia, 628.
Magnesia alba, 639
Magnesite, 625, 637
Magnesium, 623; atomic weight of, 642: compounds of, 628; detection of, 641; estimation of, 641; preparation of, 625; properties of, 627
Magnesium bromide, 632
Magnesium carbides, 637
Magnesium carbonates, 637
Magnesium chloride, 630
Magnesium cobaltite, 1281
Magnesium ferrite, 1225
Magnesium ferrocyanide, 1256
Magnesium fluoride, 630
Magnesium hydroxide, 629
Magnesium iodide, 632
Magnesium molybdate, 1069
Magnesium nitrate, 636
Magnesium nitride, 635
Magnesium oxide, 628
Magnesium oxychlorides, 631
Magnesium peroxide, 630
Magnesium phosphates, 636
Magnesium phosphide, 636
Magnesium platinocyanide, 1403
Magnesium silicates, 640
Magnesium silicide, 640
Magnesium sulphate, 195, 633
Magnesium sulphide, 632
Magnetic iron ore, 1165, 1174, 1177
Magnetic oxide of iron, 106, 1219
Magnetic pyrites, 1165, 1234, 1298
Magnetite, 1174
Magnoferrite, 629
Malachite, 400, 440
Manganates, 1139
Manganese, 1123; alloys of, 1127; atomic weight of, 1159; detection of, 1157; estimation of, 1158; preparation of, 1124; properties of, 1127
Manganese alums, 1151
Manganese antimonide, 1154
Manganese arsenides, 1154
Manganese borate, 1154
Manganese borides, 1154
Manganese bronze, 1127
Manganese carbide, 1155
Manganese carbonate, 1155
Manganese chromite, 1025
Manganese dioxide, 1132; regeneration of, 1134
Manganese disulphide, 1150
Manganese heptoxide, 1140
Manganese nitrate, 1153
Manganese nitride, 1152
Manganese ores, valuation of, 1159
Manganese phosphides, 1153
Manganese silicides, 1156
Manganese spar, 1124, 1155
Manganese steel, 1214
Manganese sulphide, 1148
Manganese tetrachloride, 1147
Manganese thiocyanate, 1156
Manganese trichloride, 1147
Manganese trioxide, 1139
Manganese tungstate, 1091
Manganic fluoride, 1145
Manganic hydroxide, 1131
Manganic oxide, 1131
Manganic phosphates, 1153
Manganic sulphate, 1151
Manganite, 1124, 1131
Manganites, 1133
Mangano-calcite, 530
Manganous aluminium sulphate, 1151
Manganous arsenate, 1154
Manganous bromide, 1149
Manganous chloride, 1146
Manganous dithionate, 1152
Manganous fluoride, 1145
Manganous hydroxide, 1129
Manganous iodide, 1149
Manganous oxide, 1129
Manganous phosphates, 1153
Manganous silicates, 1157
Manganous sulphate, 1150
Manganous tetriodate, 1149
Mapping spectra, 148
Marble, 530, 561
Marcasite, 998
Martensite, 1216
Mass action, law of, 128
Massicot, 886
Matlockite, 873, 892
Matt glass, 592
Meerschaum, 625
Melaconite, 400
Melting points of the elements, 61
Menachanite, 805
Mendeléeff's system, 48
Mendipite, 873, 892
Mercuric acetylide, 699
Mercuric arsenide, 698
Mercuric bromide, 691
Mercuric carbonates, 699
Mercuric chloride, 688
Mercuric compounds, 680
Mercuric cyanate, 700
Mercuric cyanide, 699
Mercuric fluoride, 688
Mercuric hyponitrite, 698
Mercuric iodide, 692, 704
Mercuric nitrate, 697
Mercuric nitrite, 698
Mercuric oxide, 682
Mercuric oxychlorides, 691
Mercuric oxycyanide, 700
Mercuric phosphide, 698
Mercuric sulphate, 696
Mercuric sulphide, 693

Mercuric thiocyanate, 700
Mercurous bromide, 685
Mercurous carbonate, 687
Mercurous chloride, 684
Mercurous compounds, 680
Mercurous fluoride, 684
Mercurous iodide, 686
Mercurous nitrate, 687
Mercurous nitrite, 686
Mercurous oxide, 682
Mercurous sulphate, 686
Mercurous sulphide, 686
Mercury, 671 ; alloys of, 678 ; ammoniacal compounds of, 700 ; atomic weights of, 706; compounds of, 680 ; detection of, 705 ; estimation of, 706 ; manufacture of, 672 ; properties of, 676 ; purification of, 675 ; world's production of, 675
Mercury and its compounds, therapeutic uses of, 703
Mercury nitride, 697
Mercury perchlorate, 693
Mercury periodide, 692
Mercury peroxide, 683
Metabisulphites, 125
Metalloids, 4
Metals, boiling points of, 62; conductivity of, 64 ; crystalline form of, 71 ; diffusion of, 86 ; melting points of, 62 ; molecular weights of, 26 ; specific heat of, 15 ; vapour density of, 26
Metals and non-metals, 4, 6
Metals of the rare earths, 69
Metals, colloidal solutions of, 72
Metastable systems, 115
Metastannic acid, 855, 857
Meteoric iron, 1163, 1298
Mica, 711
Microcosmic salt, 391
Microscopical study of alloys, 81
Millerian indices, 180
Millerite, 1298, 1308
Millon's base, 701
Milk glass, 588
Milk of lime, 535
Mimetesite, 873, 899
Minium, 888
Mispickel, 1246
Molecular heat of compounds, 21
Molecular weights of metallic compounds, 14
Molecular weights of the metals, 26
Molecule and atom, 27
Molybdenite, 1060, 1078
Molybdenum, 1059; atomic weight of, 66, 1082; detection of, 1081 ; estimation of, 1081 ; metallurgy of, 1060 ; properties of 1061
Molybdenum boride, 1080
Molybdenum carbides, 1080
Molybdenum dibromide, 1073
Molybdenum dichloride, 1073
Molybdenum di-iodide, 1073
Molybdenum dioxide, 1063
Molybdenum disulphide, 1078
Molybdenum hexafluoride, 1073
Molybdenum molybdates, 1069
Molybdenum nitride, 1080
Molybdenum oxyhalides, 1076
Molybdenum pentachloride, 1075
Molybdenum phosphide, 1080
Molybdenum sesquioxide, 1062
Molybdenum sesquisulphide, 1078
Molybdenum silicide, 1080
Molybdenum tetrabromide, 1075
Molybdenum tetrachloride, 1075
Molybdenum tetrasulphide, 1079
Molybdenum tetriodide, 1075
Molybdenum tribromide, 1075
Molybdenum trichloride, 1074
Molybdenum trioxide, 1064
Molybdenum trisulphide, 1079
Molybdenyl tetrachloride, 1076
Molybdenyl tetrafluoride, 1076
Molybdic acid, 1065
Molybdic ochre, 1060
Molybdic tetrahydroxide, 1063
Monazite, 775, 830, 831
Monel metal, 1304
Monoclinic system, 188, 201
Monosymmetric system, 188
Monthier's blue, 1263
Morphotropy, 219
Mortar, 534, 565 ; hydraulic, 565
Mosaic gold, 866
Mottramite, 912
Muntz metal, 651

N

Nagyagite, 491
Natron, 275
Natural arrangement of the elements, 44
Neodymium, 798; compounds of, 798 ; detection of, 799
Neoytterbium, 802
Neptunium, 946
Nessler's solution, 702
Niccolite, 1298, 1312
Nickel, 1297 ; alloys of, 1302 ; atomic weight of, 67, 1318 ; detection of, 1315 ; estimation of, 1316; metallurgy of, 1298 ; properties of, 1301
Nickel ammonium sulphate, 1310
Nickel and cobalt, separation of, 1316, 1317
Nickel arsenates, 1312
Nickel arsenides, 1312
Nickel blende, 1298
Nickel boride, 1312
Nickel bromide, 1308
Nickel carbonate, 1314
Nickel chlorate, 1308
Nickel chloride, 1307

Nickel cyanide, 1314
Nickel dioxide, 1306
Nickel disulphide, 1309
Nickel fluoride, 1307
Nickel glance, 1298
Nickel hydroxide, 1305
Nickel iodate, 1308
Nickel iodide, 1308
Nickel monosulphide, 1308
Nickel monoxide, 1305
Nickel nitrate, 1311
Nickel nitride, 1311
Nickel nitrite, 1311
Nickel ochre, 1298
Nickel oxides, 1304
Nickel phosphates, 1312
Nickel phosphides, 1311
Nickel plating, 1301
Nickel sesquioxide, 1306
Nickel sesquisulphide, 1309
Nickel silicates, 1315
Nickel silicide, 1314
Nickel silver, 1302, 1303
Nickel subsulphide, 1309
Nickel sulphate, 1309
Nickel tetracarbonyl, 1312
Nickel tetroxide, 1307
Nickel trihydroxide, 1306
Nickeline, 1298, 1312
Niobium, 944
Nitrates, 126
Nitre, 343
Nitrides, 126
Nitrites, 126
Nitritoplatinites, 1397
Nitrocobalt, 1286
Nitrocopper, 430
Nitronickel, 1311
Nitroprussic acid, 1266
Nitrosoferricyanic acid, 1266
Nixferrum, 975
Non-metals, 4
Normal salts, 107
Normal valency, 41

O

Odontolite, 738
Okenite, 564
Olivenite, 440
Optical activity, 197
Orangite, 830, 833
Ornithite, 558
Orthoclase, 319, 711, 739
Orthorhombic system, 189
Osmiamic acid, 1357
Osmic acid, 1352
Osmichlorides, 1354
Osminitrites, 1358
Osmiridium, 1319, 1349, 1361, 1374
Osmisulphites, 1356
Osmium, 1349; atomic weight of, 66, 1360; detection of, 1359; estimation of, 1360; preparation of, 1349; properties of, 1350
Osmium bromides, 1355
Osmium chlorides, 1354
Osmium iodides, 1355
Osmium nitrite, 1358
Osmium oxides, 1351
Osmium oxysulphide, 1352
Osmium sulphite, 1356
Osmium tetrasulphide, 1356
Osmium tetroxide, 1353
Osmochlorides, 1354
Osmocyanic acid, 1358
Osmosammine hydroxide, 1357
Osmyldiammine chloride, 1357
Osteolite, 530, 558
Oxides, 102
Oxymuriate of tin, 863

P

Packfong, 1302
Palladichlorides, 1343
Palladiochlorides, 1343
Palladium, 1336; ammoniacal compounds of, 1346; atomic weight of, 1348; detection and estimation of, 1347; preparation of, 1337; properties of, 1337
Palladium bromides, 1344
Palladium chlorides, 1342, 1343
Palladium cyanide, 1345
Palladium hydrogen, 1340
Palladium nitrate, 1345
Palladium oxides, 1339, 1340
Palladium sulphate, 1345
Palladium sulphides, 1344, 1345
Palladium thiocyanate, 1346
Parallel growths, 215
Parametral plane, 179
Parametral ratios, 179
Paris blue, 1265
Patent yellow, 893
Pateraite, 1060
Patronite, 913
Pearl-ash, 355
Pearlite, 1216
Pectolite, 565
Pelopium, 945
Pentlandite, 1298
Perchlorates, 124
Perchromic acid, 1037
Percolumbic acid, 952
Periodic system, 48, 54; anomalies of, 69
Permanent white, 607, 611
Permanganic acid, 1141
Permanganic oxychloride, 1148
Permolybdic acid, 1072
Perofskite, 806, 811
Perosmic anhydride, 1353
Peroxides, 105
Perstannic acid, 858

Pertantalic acid, 959
Perthiomolybdic acid, 1079
Pertungstic acid, 1095
Peruranates, 1111
Pervanadates, 925
Pervanadic acid, 925
Petalite, 227
Pewter, 970
Pharaoh's serpent, 700
Pharmacosiderite, 1246
Phase rule, 114
Phenacite, 617
Phosgenite, 873
Phosphides, 127
Phosphochalcite, 439
Phosphomolybdic acid, 1070
Phosphor-bronze, 851
Phosphorescence spectra, 148
Phosphotungstic acids, 1092
Phosphovanadic acid, 940
Photography, 482
Pitchblende, 1105, 1427
Plane of symmetry, 183
Plaster of Paris, 554
Platinates, 1388
Plating, 460
Platinibromic acid, 1395
Platinic acid, 1388
Platinic bromide, 1394
Platinic chloride, 1392
Platinic hydroxide, 1387
Platinic iodide, 1395
Platinic sulphate, 1396
Platinichloric acid, 1393
Platinichlorides, 123
Platiniodic acid, 1395
Platiniridium, 1361
Platinithiocyanic acid, 1403
Platinochlorides, 1391
Platinocyanic acid, 1401
Platinoid, 1304
Platinonitrites, 1397
Platinosulphites, 1396
Platinothioplatinates, 1396
Platinous bromide, 1394
Platinous chloride, 1389
Platinous fluoride, 1389
Platinous hydroxide, 1387
Platinous iodide, 1395
Platinum, 1371
Platinum, action of various reagents on, 1386; ammoniacal compounds of, 1398; atomic weight of, 66, 1406; colloidal, 1385; detection of, 1404; estimation of, 1405; fulminating, 1398; metallurgy of, 1374; preparation of pure, 1379; properties of, 1381; spongy, 1384; world's production of, 1380
Platinum arsenide, 1401
Platinum black, 1384
Platinum dioxide, 1387
Platinum monochloride, 1389
Platinum monoxide, 1387
Platinum ore, 1319, 1328, 1336, 1349, 1373, 1374
Platinum oxides, 1387
Platinum phosphides, 1400
Platinum selenide, 1397
Platinum sulphides, 1395, 1396
Platinum tellurides, 1397
Platinum trioxide, 1389
Plumbates, 890
Plumbocalcite, 530
Pollux, 372
Polonium, 1428, 1438
Polybasite, 445
Polyhalite, 330
Polymorphism, 202
Polysphaerite, 899
Porcelain, 741
Portland cement, 565
Positive rays, 1410
Potash, 225
Potash alum, 734
Potashes, 355
Potash felspar, 739
Potash lye, 327
Potassamide, 342
Potassammonium, 378
Potassium, atomic weight of, 67, 362; detection of, 361; discovery of, 318; estimation of, 362; preparation of, 320; properties of, 322; sources of, 319
Potassium amalgam, 89
Potassium amidochromate, 1037
Potassium antimonate, 978
Potassium antimonyl tartrate, 974
Potassium arsenate, 354
Potassium arsenide, 353
Potassium arsenite, 353
Potassium aurate, 512
Potassium aurichloride, 516
Potassium aurochloride, 514
Potassium aurocyanide, 523
Potassium azoimide, 342
Potassium borates, 354
Potassium bromate, 336
Potassium bromide, 331
Potassium carbide, 354
Potassium carbonate, 355
Potassium chlorate, 333
Potassium chloride, 319, 329
Potassium chlorochromate, 1036
Potassium chloroplatinicyanide, 1402
Potassium chromate, 1027
Potassium chromic sulphate, 1044
Potassium chromicyanide, 1050
Potassium chromithiocyanate, 1050
Potassium chromocyanide, 1050
Potassium chromosulphate, 1047
Potassium cobalticyanide, 1293
Potassium cobaltinitrite, 1286
Potassium cobaltocyanide, 1293
Potassium columbifluoride, 953
Potassium cyanate, 359
Potassium cyanide, 358

Potassium dichromate, 187, 1028
Potassium disulphate, 341
Potassium di-uranate, 1110
Potassium ferrocyanide, 1254, 1257
Potassium fluochromate, 1035
Potassium fluoride, 329
Potassium hexacolumbate, 951
Potassium hexatantalate, 959
Potassium hydride, 329
Potassium hydrogen carbonate, 358
Potassium hydrogen sulphate, 341
Potassium hydrogen sulphite, 340
Potassium hydrosulphide, 338
Potassium hydroxide, 325
Potassium hypoantimonate, 976
Potassium hypochlorite, 333
Potassium iodate, 336
Potassium iodide, 332
Potassium iodotetrachloride, 333
Potassium iridate, 1365
Potassium iridibromide, 1367
Potassium iridichloride, 1366
Potassium iridicyanide, 1368
Potassium iridiobromide, 1366
Potassium iridiocyanide, 1368
Potassium iridionitrite, 1368
Potassium manganate, 1140
Potassium manganichloride, 1148
Potassium manganicyanide, 1156
Potassium manganifluoride, 1145
Potassium manganocyanide, 1155
Potassium metabisulphite, 340
Potassium metaphosphate, 353
Potassium molybdates, 1067
Potassium monoxide, 324
Potassium nitrate, 343
Potassium nitrite, 343
Potassium nitroprusside, 1268
Potassium orthophosphate, 352
Potassium osmate, 1352
Potassium osmiamate, 1357
Potassium osmichloride, 1354
Potassium osmochloride, 1354
Potassium osmocyanide, 1358
Potassium osmyl chloride, 1355
Potassium palladichloride, 1343
Potassium palladiobromide, 1344
Potassium palladiochloride, 1343
Potassium palladionitrite, 1345
Potassium pentathiomolybdate, 1079
Potassium perborate, 354
Potassium percarbonate, 358
Potassium perchlorate, 190, 214, 335
Potassium periodate, 183, 336
Potassium permanganate, 1142
Potassium peroxide, 327
Potassium per-ruthenate, 1322
Potassium persulphate, 342
Potassium pertantalate, 959
Potassium platinichloride, 1393
Potassium platinithiocyanate, 1403
Potassium platinobromide, 1394
Potassium platinochloride, 1391
Potassium platinocyanide, 1401
Potassium platinonitrite, 1397
Potassium platinothiocyanate, 1403
Potassium polysulphides, 338
Potassium pyroantimonate, 979
Potassium pyrophosphate, 353
Potassium rhodicyanide, 1334
Potassium ruthenate, 1322
Potassium ruthenichloride, 1324
Potassium ruthenio-cyanide, 1327
Potassium selenate, 342
Potassium silicates, 360
Potassium silicofluoride, 361
Potassium silicotungstates, 1094
Potassium stannate, 856
Potassium stannifluoride, 862
Potassium sulphate, 189, 214, 218, 340
Potassium sulphide, 337
Potassium sulphite, 339
Potassium sulpho-carbonate, 358
Potassium tantalofluoride, 960
Potassium tetrachromate, 1030
Potassium thioantimonate, 990
Potassium thiomolybdate, 1079
Potassium thiocyanate, 360
Potassium thiostannate, 867
Potassium thiosulphate, 342
Potassium thorofluoride, 835
Potassium titanate, 811
Potassium titanofluoride, 813
Potassium triantimonite, 976
Potassium trichromate, 1030
Potassium tri-iodide, 332
Potassium tungstates, 1089
Potassium vanadite, 929
Potassium zirconofluoride, 825
Pottery, 741
Powder of Algaroth, 982
Praseodymium, 796; compounds of, 797; detection of, 798
Prediction of undiscovered elements, 68
Preparing salts, 856
Principal valency, 37
Proustite, 445
Prout's hypothesis, 42
Prussian blue, 1249, 1261, 1262, 1263, 1265
Prussian green, 1265
Prussiate of potash, red, 1257; yellow, 1254
Pseudomalachite, 439
Pseudoracemic compounds, 211
Psilomelane, 602, 1124
Psittacinite, 912
Pucherite, 912, 999
Puddling process, 1193
Purple of Cassius, 508
Puzzuolana, 565
Pyrargyrite, 445, 964
Pyritic smelting, 410
Pyrochlor, 830, 947
Pyrolusite, 1124, 1132, 1159
Pyromorphite, 873, 899

Q

Quadratic system, 190
Quartation, 87
Quartz, 196
Quicksilver, 671

R

Racemic substances, 211
Radioactive change, products of, 1424; rate of, 1425
Radioactive elements, 1407, 1444
Radioactive elements and the periodic system, 1426, 1429
Radioactive substances, discovery of, 1413
Radioactivity, measurement of, 1414; phenomena of, 1416
Radiotellurium, 1438
Radium, 1427; atomic weight of, 1431; emanation, 1424, 1434; heat emission by, 1423, 1436; spectrum of, 1430; spontaneous change of, 1432; transformation products of, 1437, 1438
Radium and uranium, 1442
Radium clock, 1420
Radium salts, preparation and properties of, 1428
Rare earths, 772; metals of the, 69; separation of, 777
Reaction velocity, 131
Reaction velocity and temperature, 137
Recalescence of steel, 1215
Red copper ore, 400, 421
Red lead, 106, 888
Red precipitate, 682
Red silver ore, 964
Regular system, 193
Regulus of Venus, 971
Reversible reactions, 128
Rewdanskite, 1298, 1315
Rheostan, 1304
Rhodites, 1332
Rhodium, 1328; ammoniacal derivatives of, 1334; atomic weight of, 1335; detection and estimation of, 1335; preparation of, 1328; properties of, 1330
Rhodium alums, 1334
Rhodium chloride, 1332
Rhodium hydroxides, 1331, 1332
Rhodium nitrate, 1334
Rhodium nitrite, 1334
Rhodium oxides, 1331, 1332
Rhodium sulphate, 1334
Rhodium sulphides, 1333
Rhodium sulphite, 1333
Rhodochlorides, 1333
Rhodocrozite, 1124, 1155
Rhodonite, 1157
Rhombic system, 189, 201
Rhombohedral system, 191, 201
Rinmann's green, 1295
Ripidolite, 711
Rock salt, 250
Römerite, 1240
Romeite, 977
Roscoelite, 912
Rose's metal, 1003
Rosin-blende, 644
Rotatory polarisation, 197
Rubidium, 364; atomic weight of, 371; detection of, 371; discovery of, 161; estimation of, 371; occurrence of, 162, 364; preparation of, 368; properties of, 369; separation of, 366
Rubidium carbonate, 371
Rubidium chlorate, 370
Rubidium chloride, 369
Rubidium hydride, 369
Rubidium hydroxide, 369
Rubidium nitrate, 370
Rubidium oxides, 369
Rubidium perchlorate, 370
Rubidium platinichloride, 1393
Rubidium selenate, 370
Rubidium sulphate, 218, 370
Rubidium sulphides, 370
Ruby, 710, 719
Ruby glass, 588
Rusting of iron, 1168
Rutheniochlorides, 1324
Rutheniocyanic acid, 1327
Ruthenium, 1319; ammoniacal derivatives of, 1326; atomic weight of, 1328; detection and estimation of, 1328; preparation of, 1319; properties of, 1320
Ruthenium bromide, 1325
Ruthenium chlorides, 1324
Ruthenium dithionate, 1325
Ruthenium hydroxides, 1321, 1322
Ruthenium iodide, 1325
Ruthenium nitrosochloride, 1326
Ruthenium oxides, 1321, 1322, 1323
Ruthenium oxychloride, 1325
Ruthenium silicide, 1327
Ruthenium sulphate, 1326
Ruthenium sulphides, 1325
Ruthenium sulphite, 1325
Rutile, 805, 806, 809

S

Salammoniac, 380
Salt-cake, 258
Salt-cake process, 288
Saltpetre, 343
Saltpetre, Chili, 262
Salts, acid, 108; basic, 108; complex, 109; double, 109, 118; fusibility

and volatility of, 121 ; generic properties of, 122 ; normal, 107 ; solubility of, 110
Salts, acids, and bases, 90
Sal-volatile, 391
Samarium, 799
Samarskite, 774, 776, 1105
Sapphire, 710, 719
Saxifragin, 613
Scandium, 68, 781 ; compounds of, 782
Scheele's green, 440
Scheelite, 1083, 1090
Schlippe's salt, 990
Schorlomite, 806
Schweizer's reagent, 424
Selenite, 530, 552
Sellaïte, 630
Senarmontite, 193
Siderite, 1175
Silicotungstic acids, 1093
Silver, 445 ; alloys of, 462 ; atomic weight of, 490 ; colloidal, 459 ; detection of, 488 ; electric refining of, 455 ; electro-deposition of, 461 ; estimation of, 489 ; metallurgy of, 445 ; molecular, 457 ; ores of, 445 ; preparation of pure, 456 ; properties of, 458 ; wet extraction of, 453 ; world's production of, 456
Silver acetylide, 481
Silver alum, 736
Silver amide, 478
Silver arsenate, 481
Silver arsenite, 481
Silver azoimide, 478
Silver biphosphide, 480
Silver bromide, 471
Silver carbide, 481
Silver carbonate, 481
Silver chlorate, 475
Silver chloride, 467
Silver chlorite, 474
Silver chromate, 1032
Silver coin, 463
Silver cyanamide, 482
Silver cyanate, 482
Silver cyanide, 482
Silver dichromate, 1032
Silver disulphide, 476
Silver fluoride, 467
Silver glance, 445
Silver hyponitrite, 478
Silver iodide, 473
Silver nitrate, 479
Silver nitride, 478
Silver nitrite, 479
Silver oxide, 464
Silver permanganate, 1144
Silver peroxide, 465
Silver phosphates, 481
Silver platinonitrite, 1397
Silver sodium thiosulphate, 477
Silver subfluoride, 466
Silver sulphate, 476
Silver sulphide, 475
Silver sulphite, 476
Silver thiocyanate, 482
Silver thiosulphate, 477
Silver ultramarine, 748
Silvering, 460, 462
Skutterudite, 1275, 1291
Slaked lime, 535
Smalt, 1295
Smaltite, 1275, 1291
Smithsonite, 644
Soda, 225, 281 ; manufacture of, 282, 303
Soda ash, 274, 299
Soda by electrolytic processes, 311
Soda crystals, 275, 316
Soda from cryolite, 303
Soda glass, soluble, 278
Sodamide, 261
Sodammonium, 378
Sodium, 237 ; atomic weight of, 280 ; compounds of, 243 ; detection of, 279 ; estimation of, 279 ; manufacture of, 239 ; occurrence of, 238 ; properties of, 242 ; spectroscopic detection of, 159 ; uses of, 243
Sodium alum, 736
Sodium aluminate, 724
Sodium aluminium chloride, 727
Sodium amalgam, 89, 678
Sodium antimonate, 979
Sodium antimonite, 976
Sodium arsenates, 269
Sodium arsenide, 269
Sodium aurichloride, 516
Sodium aurothiosulphate, 520
Sodium azoimide, 262
Sodium bicarbonate, 275, 316
Sodium borates, 270
Sodium bromide, 253
Sodium carbide, 273
Sodium carbonate, 274
Sodium chlorate, 255
Sodium chloride, 250
Sodium chromate, 1030
Sodium cyanide, 277
Sodium dichromate, 1031
Sodium dioxide, 246
Sodium disulphate, 260
Sodium di-uranate, 1110
Sodium ferricyanide, 1258
Sodium ferrocyanide, 1255
Sodium fluoride, 249
Sodium hexatantalate, 959
Sodium hydride, 249
Sodium hydrogen sulphate, 260
Sodium hydrogen sulphite, 258
Sodium hydroxide, 244
Sodium hypochlorite, 253
Sodium hypophosphite, 264
Sodium hyposulphite, 256
Sodium iodide, 253
Sodium iridichloride, 1366

Sodium manganate, 1140
Sodium metabisulphite, 258
Sodium molybdates, 1066
Sodium monoxide, 244
Sodium metaphosphates, 267
Sodium metastannate, 857
Sodium nitrate, 191, 262
Sodium nitrite, 262
Sodium nitroprusside, 1268
Sodium orthophosphates, 264
Sodium osmate, 1352
Sodium osmichloride, 1355
Sodium osminitrite, 1358
Sodium osmisulphite, 1356
Sodium palladiosulphite, 1345
Sodium percarbonate, 277
Sodium perchlorate, 256
Sodium permanganate, 1144
Sodium peruranate, 1111
Sodium phosphide, 264
Sodium platinichloride, 1393
Sodium pyroantimonate, 979
Sodium pyrophosphates, 267
Sodium rhodochloride, 1333
Sodium seleno-antimonate, 993
Sodium sesquicarbonate, 317
Sodium silicates, 277
Sodium silicofluoride, 279
Sodium stannate, 856
Sodium suboxide, 243
Sodium sulphate, 258; solubility of, 115
Sodium sulphides, 256
Sodium sulphonosmate, 1356
Sodium sulphite, 257
Sodium tantalofluoride, 960
Sodium thioantimonate, 990
Sodium thiopalladate, 1345
Sodium thiostannate, 867
Sodium thiosulphate, 260
Sodium titanofluoride, 814
Sodium trioxide, 249
Sodium tungstates, 1089
Sodium vanadite, 929
Sodium zirconate, 825
Soft soap, 327
Solar atmosphere, 168
Solar spectrum, 168
Solder, 850
Sollas' theory, 222
Soluble soda glass, 278
Solubility of alloys, 87; of salts, 110
Solvay's apparatus, 306
Sombrerite, 558
Sorawallahs, 344
Sorbite, 1216
Spark spectra, 146
Spathic iron ore, 1165, 1175, 1177, 1247
Spectra, 145, 146, 148, 152, 154, 157, 163, 171
Spectral lines, relations between 155
Spectroscope, 143
Spectroscope and chemical analysis, 158
Spectrum analysis, 139
Specular iron ore, 1165, 1174
Speculum-metal, 850
Specific gravity of the elements, 57
Specific heat of metals, 15
Speiss-cobalt, 1275
Sperrylite, 1373
Sphene, 806, 812
Spiegel iron, 1188
Spinel, 625, 724
Spodumene, 227
Stannibromides, 865
Stannic acid, 855, 856, 858
Stannic bromide, 865
Stannic chloride, 862
Stannic fluoride, 861
Stannic hydroxides, 855
Stannic iodide, 865
Stannic nitrate, 868
Stannic oxide, 854
Stannic oxysulphide, 868
Stannic pyrophosphate, 869
Stannic sulphate, 868
Stannic sulphide, 866
Stannichlorides, 864
Stannifluorides, 862
Stannous bromide, 860
Stannous chloride, 859
Stannous fluoride, 859
Stannous iodide, 860
Stannous nitrate, 861
Stannous oxide, 853
Stannous sulphate, 861
Stannous sulphide, 860
Stassfurt minerals, 119
Stassfurt salts, 330
Steel, 1172, 1198, 1212, 1214, 1215
Steel bronze, 718
Stellar spectra, 171
Stephanite, 445
Stibine, 971
Stiblite, 964
Stibnite, 962, 985
Stolzite, 873, 1083, 1091
Stoneware, 745
Stourbridge clay, 740
Stream-tin, 854
Stromeyerite, 445
Strontia, 597
Strontianite, 594
Strontium, 594; atomic weight of, 600; compounds of, 596; detection of, 599; estimation of, 600; preparation of, 595; properties of, 596
Strontium arsenide, 599
Strontium boride, 599
Strontium carbonate, 599
Strontium chloride, 597
Strontium ferrocyanide, 1256
Strontium hydride, 597
Strontium hydroxide, 597

Strontium nitrate, 598
Strontium nitride, 599
Strontium oxides, 597
Strontium phosphide, 599
Strontium sulphate, 598
Strontium sulphide, 598
Suboxides, 106
Suint, 320
Sulphates, 125
Sulphides, 124
Sulphites, 125
Sulphochromic hydroxide, 1048
Sulphochromites, 1048
Sulphonosmates, 1356
Sulphur, 203
Sulvanite, 913
Superphosphate of lime, 559
Supersaturated solutions, 120
Supersaturation, 215
Supersolubility curve, 120
Supplementary valency, 37
Sylvanite, 491
Sylvine, 319, 330
Symmetry of crystals, 182
Sympathetic inks, 1282

T

Tachhydrite, 330, 537, 631
Tachyol, 467
Talc, 625
Tantalates, 959
Tantalic acid, 958
Tantalite, 944, 946, 948
Tantalum, 957; atomic weight of, 962; detection of, 962; preparation of, 957; properties of, 957
Tantalum carbide, 962
Tantalum compounds, extraction of, 948
Tantalum dichloride, 961
Tantalum nitrides, 961
Tantalum oxides, 958
Tantalum pentabromide, 961
Tantalum pentachloride, 960
Tantalum pentafluoride, 960
Tantalum sulphide, 961
Tartar emetic, 974, 994
Telluric bismuth, 999
Tellurium, atomic weight of, 67
Tenorite, 400
Tephroite, 1157
Terbium, 801
Tesseral system, 193
Tetradymite, 999, 1011
Tetragonal system, 190, 201
Thallic bromide, 769
Thallic chloride, 768
Thallic hydroxide, 767
Thallic nitrate, 770
Thallic sulphate, 769
Thallic sulphide, 769
Thallium, 759; atomic weight of, 771; compounds of, 761; detection of, 770; discovery of, 162; estimation of, 770; preparation of, 760; properties of, 760
Thallium alum, 764
Thallium monoxide, 761
Thallium phosphates, 765
Thallium silicate, 766
Thallium trioxide, 767
Thallous bromide, 763
Thallous carbonate, 766
Thallous chlorate, 763
Thallous chloride, 762
Thallous cyanide, 766
Thallous fluoride, 762
Thallous hydroxide, 762
Thallous iodide, 763
Thallous nitrate, 765
Thallous perchlorate, 763
Thallous sulphate, 764
Thallous sulphide, 764
Thénard's blue, 1295
Thermal classification of alloys, 77
Thermite, 716
Thermonatrite, 275
Thiostannic acid, 867
Thiotungstate, 1101
Thoria, 833
Thorianite, 775, 830, 831
Thorite, 830, 831, 833
Thorium, 830
Thorium, atomic weight of, 837; compounds of, 833; detection of, 837; estimation of, 837; preparation of, 832; properties of, 833; radioactivity of, 1440
Thorium borides, 836
Thorium carbide, 836
Thorium chloride, 835
Thorium fluoride, 834
Thorium hydride, 834
Thorium nitrate, 832, 836
Thorium nitride, 836
Thorium oxides, 833, 834
Thorium phosphate, 836
Thorium silicide, 837
Thorium sulphate, 836
Thorium sulphide, 835
Thulium, 801
Tin, 841
Tin, alloys of, 850; atomic weight of, 871; compounds of, 853; detection of, 869; estimation of, 870; metallurgy of, 843; properties of, 848; uses of, 849
Tin amalgam, 851
Tin peroxide, 858
Tin phosphides, 869
Tin pyrites, 843
Tin salt, 859
Tincal, 271
Tinstone, 843, 854
Titanic acids, 810

Titanic iron ore, 812
Titanite, 806, 812
Titanium, 805 ; atomic weight of, 821 ; compounds of, 808 ; detection of, 820 ; estimation of, 821 ; preparation of, 806 ; properties of, 807
Titanium bromides, 816
Titanium carbide, 819
Titanium chlorides, 814
Titanium cyanonitride, 819
Titanium dichloride, 814
Titanium fluorides, 813
Titanium iodides, 817
Titanium nitrides, 819
Titanium oxides, 808
Titanium oxychloride, 816
Titanium sulphates, 818
Titanium sulphides, 817
Titanium tetrachloride, 815
Titanium trichloride, 814
Titanium trioxide, 812
Tiza, 271
Tombac, 651
Topaz, 739
Topic axes, 218
Transition interval, 118
Transition temperature, 113
Trichromyl chloride, 1036
Triclinic system, 187, 201
Trigonal system, 191
Trimanganese tetroxide, 1130
Triphane, 227
Triphylite, 227, 365
Trögerite, 1120
Troilite, 1232
Trona, 276
Troostite, 1216
Tungsten, 1082 ; atomic weight of, 1104 ; detection of, 1103 ; estimation of, 1103 ; preparation of, 1083 ; properties of, 1084
Tungsten arsenide, 1102
Tungsten boride, 1103
Tungsten bronzes, 1091
Tungsten carbides, 1102
Tungsten chlorosulphide, 1101
Tungsten dibromide, 1100
Tungsten dichloride, 1096
Tungsten di-iodide, 1101
Tungsten dioxide, 1085
Tungsten disulphide, 1101
Tungsten hexabromide, 1100
Tungsten hexachloride, 1098
Tungsten hexafluoride, 1095
Tungsten nitride, 1102
Tungsten oxybromides, 1100
Tungsten oxychlorides, 1099
Tungsten oxyfluorides, 1096
Tungsten pentabromide, 1100
Tungsten pentachloride, 1097
Tungsten phosphides, 1102
Tungsten silicide, 1103
Tungsten tetrachloride, 1097
Tungsten tetra-iodide, 1101
Tungsten trioxide, 1086
Tungsten trisulphide, 1101
Tungsten tungstates, 1091
Tungstic acid, 1087
Tungstosilicic acid, 1094
Turnbull's blue, 1264
Turner's yellow, 893
Turquoise, 738
Twin crystals, 197
Type metal, 970

U

Ullmannite, 964
Ultramarine, 746
Uranates, 1110
Uranic hydroxide, 1109
Uranic oxide, 1109
Uraninite, 1105
Uranite, 1105
Uranium, 1104 ; atomic weight of, 67, 1121 ; detection of, 1120 ; estimation of, 1121 ; preparation of, 1106 ; properties of, 1107 ; radioactivity of, 1441
Uranium and radium, 1442
Uranium arsenide, 1119
Uranium carbide, 1120
Uranium dioxide, 1108
Uranium hexafluoride, 1112
Uranium mica, 1105
Uranium nitride, 1118
Uranium oxybromide, 1115
Uranium oxychloride, 1114
Uranium pentachloride, 1114
Uranium pentoxide, 1111
Uranium peroxide, 1111
Uranium phosphide, 1119
Uranium red, 1117
Uranium selenides, 1117
Uranium sesquisulphide, 1116
Uranium telluride, 1117
Uranium tetrabromide, 1115
Uranium tetrachloride, 1113
Uranium tetrafluoride, 1112
Uranium tetraiodide, 1115
Uranium trichloride, 1113
Uranoso-uranic oxide, 1111
Uranospinite, 1120
Uranotantalite, 1105
Uranothallite, 1105
Uranous chloride, 1113
Uranous fluoride, 1112
Uranous hydroxide, 1109
Uranous oxyfluoride, 1113
Uranous phosphates, 1119
Uranous sulphate, 1117
Uranous sulphide, 1116
Uranyl arsenates, 1119
Uranyl bromide, 1115
Uranyl carbonates, 1120
Uranyl chloride, 1114

Uranyl fluoride, 1112
Uranyl iodide, 1116
Uranyl nitrate, 1119
Uranyl oxide, 1109
Uranyl phosphates, 1119
Uranyl selenide, 1117
Uranyl sulphate, 1118
Uranyl sulphide, 1116
Uranyl sulphite, 1117
Urao, 276

V

Valency, 27, 36, 39, 41, 55
Valency volume theory, 220
Valentinite, 964, 974
Vanadates, 920
Vanadic acids, 920
Vanadic anhydride, 918
Vanadinite, 912
Vanadious sulphate, 936
Vanadites, 929
Vanadium, 911; atomic weight of, 943; detection of, 941; estimation of, 942; preparation of, 913; properties of, 917
Vanadium alums, 937
Vanadium carbide, 940
Vanadium chlorides, 931
Vanadium cyanides, 941
Vanadium dichloride, 932
Vanadium dioxide, 928
Vanadium fluorides, 930
Vanadium group, 911
Vanadium monoxide, 926
Vanadium nitrides, 939
Vanadium oxides, 918
Vanadium oxychlorides, 931
Vanadium sesquioxide, 928
Vanadium sesquisulphate, 937
Vanadium silicides, 941
Vanadium suboxide, 926
Vanadium sulphides, 935
Vanadium tetrachloride, 931
Vanadium thiocyanates, 941
Vanadium tribromide, 934
Vanadium trichloride, 932
Vanadyl bromides, 935
Vanadyl chlorides, 934
Vanadyl sulphates, 938
Vanadyl sulphite, 936
Vanadyl trichloride, 933
Vapour density of metallic compounds, 14, 31
Vauquelinite, 1032
Velocity coefficient, 131
Velocity of reaction, 131
Venetian white, 903
Vermilion, 694
Vitriol, green, 1236
Vitriol ochre, 1239
Vivianite, 1245
Voglite, 1105
Volborthite, 912

W

Wad, 1275
Walpurgite, 1120
Washing soda, 275
Websterite, 730
Weldon process, 1134
Werner's theory of valency, 36
White lead, 900
White metal, 971
White precipitate, 702
Williamson's violet, 1262
Witherite, 602, 613
Wolfram, 1083, 1091
Wolframinium, 718
Wolframochre, 1083
Wolfsbergite, 964
Wollastonite, 564
Wood, ashes of, 355
Wood-tin, 854
Wood's metal, 1003
Wrought iron, 1172, 1189, 1197
Wulfenite, 873, 1060
Wurtzite, 657

X

Xenotime, 775
Xonalite, 564

Y

Yellow ultramarine, 1032
Yttrium, 782; atomic weight of, 784; compounds of, 783, 784; detection of, 784
Yttrotantalite, 947

Z

Zaffre, 1275, 1292
Zinc, 642; alloys of, 651; ammoniacal derivatives of, 661; atomic weight of, 663; compounds of, 652; detection of, 662; estimation of, 663; properties of, 648; smelting of, 644; uses of, 650
Zinc amide, 660
Zinc blende, 644
Zinc bromide, 656
Zinc carbonates, 660
Zinc chloride, 655
Zinc chromates, 1032
Zinc chromite, 1025
Zinc cyanide, 661
Zinc dust, 650
Zinc ferrite, 1225
Zinc ferrocyanide, 1256
Zinc hydrazide, 660
Zinc hydroxide, 653

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Zircon, 191, 214, 822, 823, 828
Zirconium, 822; atomic weight of, 829; detection of, 829; estimation of, 829; preparation of, 822; properties of, 823
Zirconium boride, 828
Zirconium bromide, 826
Zirconium carbides, 828
Zirconium chloride, 826
Zirconium fluoride, 825
Zirconium iodide, 827
Zirconium nitrate, 828
Zirconium nitrides, 827
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